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## Some polynuclear tantalum halides and their oxidized derivatives

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THEIR OXIDIZED DERIVATIVES.

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SOME POLYNUCLEAR TANTALUM HALIDES  
AND THEIR OXIDIZED DERIVATIVES

by

Benjamin Glenn Hughes

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

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In Charge of Major Work

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Dean of Graduate College

Iowa State University  
Of Science and Technology  
Ames, Iowa

1964

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## INTRODUCTION

The preparation and identification of lower halides of the Group V and VI heavy transition metals which form stable aqueous solutions have been reported in the literature for many years. Recent studies have positively identified these soluble compounds as polynuclear halides which yield ions in solution of the form  $M_6X_8^{+4}$  and  $M_6X_{12}^{+2}$  (where M = Mo, W, Nb, Ta; X = Cl, Br, I).

Current interests in metal atom clusters of this type have pointed up the need for more knowledge of their basic chemical and physical properties. While the molybdenum compounds have been and are still being studied, the tantalum and niobium polynuclear halides have been largely neglected in this respect.

Recent work in this laboratory (1) has provided a means for obtaining the polynuclear tantalum halides in large quantities. The present work is intended to take advantage of this opportunity to begin investigations into the varied and unusual chemistry of these unique tantalum compounds.

## Chemistry of the Polynuclear Metal Halides

### Polynuclear tantalum halides

Studies of the chemistry of the polynuclear tantalum halides appear infrequently in the literature. Most references to chemical reactions for these compounds are given as partial proof of a preparation and are generally simple observations rather than detailed investigations of chemical properties.

In 1907 Chabrié (2) reported the synthesis of a green crystalline powder by reduction of tantalum(V) chloride with sodium amalgam. The product was soluble in hot dilute hydrochloric acid to give a green solution and was thermally decomposed to yield tantalum(V) oxide. Analysis of a product crystallized from aqueous solution gave the composition  $\text{TaCl}_2 \cdot 2\text{H}_2\text{O}$ .

A number of interesting reactions were observed for the green solution. Addition of nitric acid to the green solution caused formation of a red-brown precipitate which redissolved in an acidic solution of tin(II) chloride to reproduce the green color. With bromine water the green solution turned yellow and was converted back to green by the action of tin(II) chloride. Treatment with nitric acid followed by

ammonia solution gave a brown precipitate. Prolonged heating with bromine gave the tantalum(V) oxide. No discussion of these reactions was presented beyond a brief statement of the observed color changes and precipitations.

Chapin (3) in 1910 used the same procedure of reduction with sodium amalgam to produce a lower bromide of tantalum which was soluble in hydrobromic acid to give an intensely green solution. A solid crystalline hydrate was obtained by evaporation of such a solution and analysis indicated the formula  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2 \cdot 7\text{H}_2\text{O}$ .

In support of his formulation, Chapin proved that one-seventh of the bromide could be precipitated with silver nitrate at  $0^\circ$  and could be exchanged for hydroxide, chloride, and iodide to yield  $(\text{Ta}_6\text{Br}_{12})(\text{OH})_2 \cdot 10\text{H}_2\text{O}$ ,  $(\text{Ta}_6\text{Br}_{12})\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ , and  $(\text{Ta}_6\text{Br}_{12})\text{I}_2 \cdot 7\text{H}_2\text{O}$  respectively. Chapin then went on to prepare a sample of the chloride reported by Chabri  and proved by analysis that it was  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2 \cdot 7\text{H}_2\text{O}$  in direct analogy to his bromide.

In 1922 Ruff and Thomas (4,5) reported the synthesis of a compound they called  $\text{TaCl}_3$ . The product was formed by reduction of tantalum(V) chloride with aluminum powder at  $300^\circ$  followed by heating at  $350^\circ$  to  $400^\circ$ . The compound was

soluble in hydrochloric or sulfuric acid to give a green solution which was apparently quite stable in air. However, it was oxidized rapidly by nitric acid, hydrogen peroxide or chlorine water to give a light brown precipitate.

Several reagents were added to samples of the green solution and observed precipitations and color changes were reported. Sodium hydroxide and ammonia solutions produced flocculent green precipitates; sodium phosphate, potassium ferrocyanide, sodium borate, and potassium fluoride caused no observable change; sodium carbonate, sodium bicarbonate, and sodium sulfide produced precipitates of the "tantalum hydroxide (Ta III)"; ammonium sulfide produced a deep olive green precipitate which dissolved in hydrochloric acid without gas evolution; and potassium oxalate and potassium cyanide produced dark green precipitates which redissolved in excess reagent. No quantitative data or analyses of any type were given.

Work done by Lindner and Feit (6,7) in 1922 and 1924 seemed to contradict the findings reported by Ruff and Thomas. They prepared a lower tantalum chloride by reducing tantalum(V) chloride with metallic lead at  $600^{\circ}$  under a stream of nitrogen. The product was extracted with hot



dilute hydrochloric acid, the lead was precipitated as  $\text{PbCl}_2$  and  $\text{PbSO}_4$ , and the solution was evaporated to precipitate hexagonal crystals of a compound formulated as  $\text{H}(\text{Ta}_3\text{Cl}_{17}\text{H}_2\text{O}) \cdot 3\text{H}_2\text{O}$  which is a compound of Ta(II). They went on to report the preparation of various pyridine, alcohol, bromide, hydroxide and sulfate derivatives all conforming to the proposed basic structural unit,  $(\text{Ta}_3\text{Cl}_{17})^-$ .

The announcement of their findings with its inferred criticism prompted a reply from Ruff and Thomas (8) maintaining the green solutions were tantalum(III). They stated that the compound reported by Lindner and Feit was more likely  $\text{Ta}_3\text{Cl}_{17}\text{O} \cdot 3\text{H}_2\text{O}$  with associated differences in the derivatives.

This, in turn, brought an answer from Lindner (9) in which he stated that the formulation  $\text{H}(\text{Ta}_3\text{Cl}_{17}\text{H}_2\text{O}) \cdot 3\text{H}_2\text{O}$  was correct and offered oxidation titrations with permanganate as proof of the presence of tantalum as tantalum(II).

A period of 25 years separates this heated discussion of the lower tantalum halides from the next and last published investigation containing any reference to chemical properties. In 1952 Young and Brubaker (10) reported the titration of a green solution of a lower tantalum chloride with cerium(IV). The material was prepared by reduction of tantalum(V)

chloride with tantalum metal at  $457^{\circ}$  to  $500^{\circ}$ . The aqueous solution gave an average oxidation state for tantalum of 3.29 and the authors considered it to be a mixture of tantalum-(III) and a compound such as  $Ta_3Cl_{10}$ .

It is interesting to note that later workers apparently ignored the observations and ideas reported by Chabri  and Chapin. It seems ironic that these earliest workers actually came closest to describing the polynuclear tantalum halides as they are characterized today.

#### Polynuclear molybdenum and tungsten halides

Blomstrand (11) reported the first synthesis of molybdenum(II) chloride and bromide in 1859. The products were prepared by volatilizing molybdenum(III) halide in a stream of carbon dioxide, dissolving the volatile product in alkali and precipitating a yellow compound with acid which gave the formula  $Mo_3X_4(OH)_2$  on analysis. Recrystallization from hydrohalic acids gave compounds of the formula  $Mo_3X_6 \cdot 6H_2O$ .

In 1898 Muthmann and Nagel (12) determined the molecular weight of the chloride by boiling point elevation in absolute alcohol and indicated the trimer as the correct formulation.

The preparation of a molybdenum(II) chloride formulated as  $(Mo_3Cl_6H_2O) \cdot HCl \cdot 3H_2O$  was reported in 1910 by Rosenheim

and Kohn (13). The formulation given was indicated by the rapid loss of three waters at 100° with only slow loss of the fourth water at 200°. The yellow needles of the compound were soluble in hydrochloric acid but hydrolyzed in pure water. The authors indicated that three-sevenths of the chloride was ionized. They succeeded in preparing pyridine and ammonium salts of the type  $(\text{NH}_4)\text{Mo}_3\text{Cl}_7(\text{NH}_3)$ .

The preparation of a compound formulated as  $\text{W}_6\text{Cl}_{12} \cdot 2\text{HCl} \cdot 9\text{H}_2\text{O}$  was discussed in 1916 by Hill (14). The compound was prepared by reduction of tungsten(VI) chloride with sodium amalgam followed by multiple extractions with alcohol-ether mixtures and recrystallizations from hydrochloric acid solution. The product, in the form of yellow needles, was readily soluble in alcohols, acetone, glacial acetic acid, and ether-alcohol mixtures. It was insoluble in pure ether, benzene, carbon disulfide, carbon tetrachloride, and chloroform. Warm nitric acid decomposed it completely. Potassium hydroxide added to a yellow solution caused it to darken rapidly to a brown color. The alkaline solution could be oxidized readily to yield stable tungsten(III) and tungsten(IV) hydrates.

During the period from 1923 to 1925 Lindner et al. (15,

16,17) reported the synthesis of a series of molybdenum(II) and tungsten(II) compounds analogous to the  $\text{HTa}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$  discussed earlier. They prepared a series of adducts and salts with pyridine, alcohol, and ammonia formulated around basic units such as  $\text{Mo}_3\text{Cl}_6$  and  $(\text{Mo}_3\text{Cl}_7)^-$ . Their observations correlate with present knowledge only if these formulations are doubled to yield units of  $\text{Mo}_6\text{Cl}_{12}$  and  $(\text{Mo}_6\text{Cl}_{14})^-$ .

In like manner the compound  $(\text{Mo}_3\text{Br}_4)(\text{NO}_3)_2$  reported by Durand, Schaal, and Souchay (18) is best understood when considered to be doubled yielding  $(\text{Mo}_6\text{Br}_8)(\text{NO}_3)_4$ . The compound was prepared by bromide exchange with silver nitrate.

A series of papers by Sheldon (19-26) represents the only definitive study of the chemistry of the molybdenum(II) halides to be found in the literature.

Beginning in 1959 Sheldon observed that the  $\text{Mo}_6\text{Cl}_8$  group acts as the center of octahedral complexes of the form  $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^-$ , ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OH}$ ). Preparation of the crystalline  $(\text{H}_3\text{O})_2 [(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$  had been reported as early as 1910 (13). The corresponding hexabromo and hexaiodo derivatives were easily prepared from solutions of the chloro-acid in the appropriate hydrohalic acid. Existence of the  $[(\text{Mo}_6\text{Cl}_8)(\text{OH})_6]^-$  ion in solution was proved by titration of

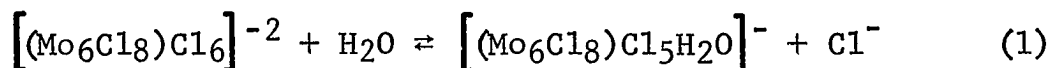
solutions of the chloro-acid in standard alkali. Molecular weight and conductivity determinations on solutions of the halo-acids indicated they were 2:1 electrolytes.

Heating of the  $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{X}_6]$ , ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), in vacuo yielded the simple molybdenum(II) halides  $(\text{Mo}_6\text{Cl}_8)\text{X}_4$  which were very hygroscopic. Studies of weight gain in air indicated the formation of tetrahydrates followed by hydrolysis with loss of hydrogen halide.

Absorption spectra for the  $\text{Mo}_6\text{Cl}_8$  compounds in  $\text{HCl}$ ,  $\text{HBr}$ , dil.  $\text{NaOH}$ ,  $\text{HClO}_4$  or  $\text{H}_2\text{SO}_4$  solution contained strong bands near 300 and 330  $\text{m}\mu$  which were relatively unaffected by the choice of solvent. Extinction coefficients indicated the bands were of the charge-transfer type with no evidence for ligand field transitions being found. These observations, coupled with the fact that  $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4$ ,  $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ , and  $(\text{NH}_4)_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$  were all found to be diamagnetic, prompted Sheldon to conclude that molybdenum exists in the octachloromolybdenum(II) group in the sexivalent state.

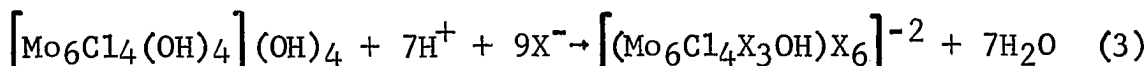
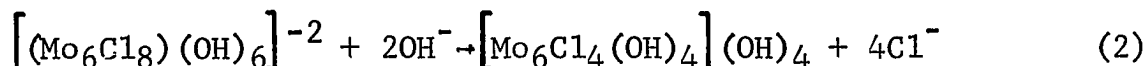
Subsequent studies of halogen exchange for  $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$  in ethanol, hydrochloric acid, and ethanolic lithium bromide solution indicated a rapid exchange of the six peripheral chloride ions with no exchange of the central

chlorides. The exchange was first order in concentration of the complex ion but independent of halide concentration. Exchange by an aquation mechanism as shown in Equation 1 was suggested.



Sheldon went on to prepare a series of ligand adducts of the  $\text{Mo}_6\text{Cl}_8$  group with triphenylphosphine oxide and triphenylarsine oxide. Both electrolytes of the form  $\left[\text{Ph}_3\text{MOH}\right]_2 \left[\text{Mo}_6\text{Cl}_8\text{Cl}_6\right]$  and non-electrolytes of the form  $\left[\text{Mo}_6\text{Cl}_8\text{Cl}_4(\text{Ph}_3\text{MO})_2\right]$  were isolated and identified. All conformed to the proposed six coordination of the  $\text{Mo}_6\text{Cl}_8$  group.

In 1961 Sheldon reported the successful substitution of hydroxide for chloride in the central  $\text{Mo}_6\text{Cl}_8$  unit. Compounds of the type  $\left[\text{Mo}_6\text{Cl}_{8-n}(\text{OH})_n\right](\text{OH})_4$  ( $n = 3$  or  $4$ ) resulted from mild alkaline hydrolysis of the  $\text{Mo}_6\text{Cl}_8$  unit. Salts such as  $(\text{Et}_4\text{N})_2 \left[\text{Mo}_6\text{Cl}_7\text{OH}\right]\text{Cl}_6$  and  $(\text{Et}_4\text{N})_2 \left[\text{Mo}_6\text{Cl}_4\text{Br}_3\text{OH}\right]\text{Br}_6$  were precipitated by adding  $\text{Et}_4\text{NCl}$  or  $\text{Et}_4\text{NBr}$  to solutions of the hydrolysis product in hydrochloric or hydrobromic acid. The proposed mechanism is shown in Equations 2 and 3.

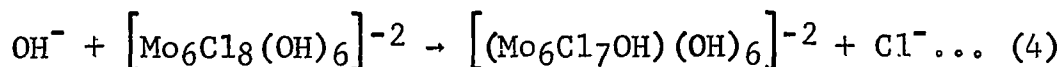


The following year Sheldon reported the preparation of

molybdenum(II) bromide and iodide by fusion of molybdenum(II) chloride with lithium bromide and iodide. From the products he prepared a series of derivatives:  $[(\text{Mo}_6\text{Br}_8)\text{X}_6]^{-2}$ ,  $[(\text{Mo}_6\text{I}_8)\text{X}_6]^{-2}$ ,  $(\text{Mo}_6\text{Br}_8)\text{X}_4$  and  $(\text{Mo}_6\text{I}_8)\text{X}_4$  (where X = Cl, Br, I, or OH). He also reported the attack by hydroxide on the iodide to yield substituted groups of the type  $[\text{Mo}_6\text{I}_{8-n}(\text{OH})_n]$ . In all respects it was apparent that these new molybdenum(II) halides were analogous to the chloride.

In the most recent of his studies Sheldon has investigated the kinetics involved in the basic hydrolysis of the  $[\text{Mo}_6\text{Cl}_8(\text{OH})_6]^{-2}$  and  $[\text{Mo}_6\text{Br}_8(\text{OH})_6]^{-2}$  ions. He found second order rate constants with the rate dependent on both complex ion and hydroxide ion concentrations. Hydrolysis of the bromide was autocatalyzed by the products of the reaction but could be controlled by destroying these products with hydrogen peroxide as they formed.

The rate of the chloride hydrolysis was much greater than the rate of the bromide hydrolysis (in the absence of catalysis). The author explains this on the basis of steric hindrance of an  $\text{S}_{\text{N}}2$  reaction with the bromide and proposes the reaction mechanism shown in Equation 4.



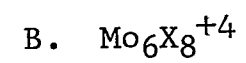
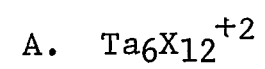
## Structure and Bonding in the Polynuclear Metal Halides

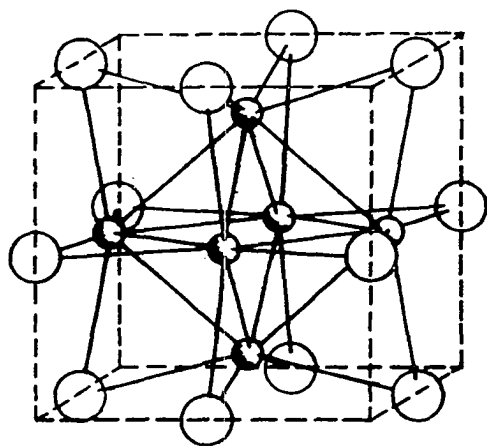
The correct structure for the polynuclear molybdenum(II) chlorides was finally established through x-ray crystallographic structure studies begun in 1946 by Brosset (27,28). He established that the compound formulated as  $(\text{Mo}_3\text{Cl}_4 \cdot 2\text{H}_2\text{O})(\text{OH})_2 \cdot 6\text{H}_2\text{O}$  was actually  $(\text{Mo}_6\text{Cl}_8)(\text{OH})_4 \cdot 14\text{H}_2\text{O}$  and the compound formulated as  $(\text{Mo}_3\text{Cl}_4 \cdot 2\text{H}_2\text{O})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  was actually  $(\text{Mo}_6\text{Cl}_8)(\text{Cl}_4 \cdot 2\text{H}_2\text{O}) \cdot 6\text{H}_2\text{O}$ . He found the lattices to be made up of  $\text{Mo}_6\text{Cl}_8$  units which were best described as a slightly distorted cube with chlorine atoms at each corner and molybdenum atoms in the face-center positions as shown in Figure 1. The molybdenum atoms then formed a nearly perfect octahedron with Mo-Mo distances of 2.62 and  $2.64\overset{\circ}{\text{A}}$  in the hydroxide and 2.69 and  $2.62\overset{\circ}{\text{A}}$  in the chloride. In each case six additional atoms of chlorine or oxygen (OH or  $\text{H}_2\text{O}$ ) were found situated on the axes perpendicular to the faces of the cube, supporting the idea of six coordination for the  $\text{Mo}_6\text{Cl}_8$  unit.

In a later work on ethanol solutions of the  $\text{Mo}_6\text{Cl}_8$  compounds, Brosset (29) used x-ray diffraction to prove the  $\text{Mo}_6\text{Cl}_8$  unit existed in solution as it had been found in the crystalline salts.



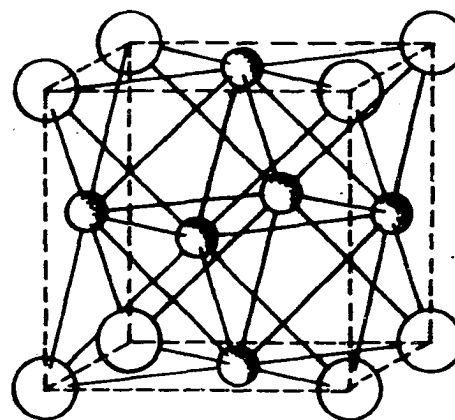
Figure 1. Structure of the polynuclear tantalum and molybdenum halide ion





**A.**

○ HALIDE  
● METAL



**B.**

In 1950 Vaughan (30) used x-ray powder diffraction data to confirm the presence of  $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{-2}$  groups in the diammonium salt, again confirming the six coordination structure for the  $\text{Mo}_6\text{Cl}_8$  unit.

In 1947 Pauling (31) discussed a number of problems in structural chemistry still unsolved at that time. In that discussion he proposed a structure for the polynuclear tantalum bromide,  $\text{Ta}_6\text{Br}_{14}$ , analogous to that observed by Brosset for the molybdenum compounds. Three years later Vaughan, Sturdivant, and Pauling (32) used x-ray diffraction by ethanolic solutions of  $\text{Ta}_6\text{Br}_{14} \cdot 7\text{H}_2\text{O}$ ,  $\text{Nb}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$ , and  $\text{Ta}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$  to prove the analogy to the molybdenum compound structure was correct. The compounds were found to exist in solutions as ions of the type  $\text{M}_6\text{X}_{12}^{+2}$  which were best described as having the metal atoms at the corners of a regular octahedron with halogen atoms on the perpendicular bisectors of the edges of the octahedron. An equivalent representation is shown in Figure 1 where the metal atoms are in the faces of a cube with halogen atoms at the center of each edge. Table 1 lists the bond distances determined from radial distribution curves obtained from the x-ray data.

Table 1. Bond distances determined for the tantalum and niobium hexanuclear halide ions

Compound	M-M $\text{\AA}$	M-X $\text{\AA}$	X-X $\text{\AA}$
$\text{Ta}_6\text{Br}_{12}^{+2}$	2.92	2.62	3.64
$\text{Ta}_6\text{Cl}_{12}^{+2}$	2.88	2.44	3.41
$\text{Nb}_6\text{Cl}_{12}^{+2}$	2.85	2.41	3.37

Bonding in the polynuclear metal halides has been discussed from both valence bond and molecular orbital approaches. Sheldon (19) considered bonding in the  $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{-2}$  compounds and proposed the formation of  $d_{x^2-y^2}sp^3$  hybrid orbitals to bind the tetragonal pyramid of chlorine atoms about each molybdenum. The  $d_{xz}$  and  $d_{yz}$  orbitals would then be directed along the intermolybdenum axes for metal-metal bonding of the  $\text{Mo}_6$  cluster.

Duffey (33) considered the possible hybridization schemes for the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  type ions and found that if bonds are considered to be directed along lines joining nearest neighbors only one spd hybrid is available and the arrangement is forbidden. However, if a distorted tetragonal antiprism arrangement is considered, eight spd hybrids can be formed, three of which overlap above each face of the

octahedron. An empty ninth orbital is left on each metal atom for bonding of a ligand to the atom cluster unit.

Gillespie (34) suggested a bonding scheme based on a distorted square antiprism configuration about each metal atom in  $M_6X_8$  and  $M_6X_{12}$  ions. To avoid bond angles he considered to be too small, he invoked the use of bent metal-halogen bonds in the structure.

Crossman, Olsen, and Duffey (35) later proposed a bonding scheme for both types of compound. They used a set of four orbitals on each metal atom for bonding the halogens, as described earlier by Duffey (33), and a resonating system of the remaining orbitals to complete the structure.

In 1964 Cotton and Haas (36) presented a molecular orbital treatment of the bonding in metal atom clusters. They observed the existence of nearly square planar  $MX_4$  units in each of the reported structures and assumed that each metal atom used a  $d_{x^2-y^2}$  or  $d_{xy}$  orbital, an s orbital, and the  $p_x$  and  $p_y$  orbitals for bonding in this square planar arrangement. They then formed the remaining d orbitals into LCAO-MO's to describe the metal-metal bonding in the clusters. Although unsatisfactory for correlation with spectra, the resulting picture indicates that all bonding levels

would be just filled leaving the  $M_6X_{12}$  units diamagnetic.

This directly contradicts the report by Krylov (37) in which the hydrates of  $Ta_6Cl_{14}$  and  $Nb_6Cl_{14}$  were reported to be weakly paramagnetic with susceptibilities which obey the Curie-Weiss law.

## EXPERIMENTAL

## Materials

Tantalum metal

Tantalum powder obtained from the National Research Corporation with a stated purity of 99.9+ was used for the preparation of all materials. Spectrographic analysis indicated the presence of the following impurities: Niobium, faint trace; chromium, faint trace; iron, weak; oxygen, 1665 ppm.; nitrogen, 220 ppm.

Aluminum metal

Aluminum in the form of thin foil was used for all reduction reactions. Spectrographic analysis indicated the presence of the following impurities in trace or faint trace amounts: Calcium, chromium, copper, iron, gallium, magnesium, manganese, nickel, silicon, and titanium.

Halogens

Reagent grade chlorine obtained in lecture-size bottles from the Matheson Co., Inc. was used for the initial preparations and subsequent oxidation procedures.

Reagent grade bromine was dried over well outgassed phosphorus(V) oxide and vacuum distilled into a clean dry flask from which it was again vacuum distilled as needed for

synthesis. Reagent grade bromine dissolved in distilled water was used for subsequent oxidation reactions.

#### Ion exchange resins

Strong anion exchange resin, Amberlite IRA-401, was obtained in the chloride form from Fisher Scientific Co. It was packed in a 2 cm. i.d. column to a depth of about 30 cm. and converted to the sulfate, perchlorate, or nitrate form by thorough washing with the appropriate 2N acid and distilled water.

Strong cation exchange resin, Amberlite IR-120 C.P., was obtained in the sodium form from Mallinckrodt Chemical Works. It was washed with distilled water until the eluate was colorless and neutral to pH paper and used without further treatment or conversion.

### Analytical Procedures

#### Tantalum

Tantalum was determined gravimetrically as the tantalum-(V) oxide. Samples were hydrolyzed in concentrated ammonia solution at the boiling point and acidified with 6N nitric acid to a pH of one. For the various bromides this procedure was sufficient to produce a pure white oxide. For the chlorides it was necessary to use higher concentrations of



nitric acid or add hydrogen peroxide in small amounts to complete the oxidation. Either method produced a colorless solution above a pure white oxide. The hydrogen peroxide procedure was preferred to avoid the possible loss of hydrogen chloride from the highly acidic solutions.

The oxide thus obtained was collected by filtration on medium porosity filter paper and dried in an oven at 120°. The filter paper was carefully burned away over a Meker burner, and the tantalum(V) oxide was ignited in a muffle furnace at 800°.

#### Halogens

Filtrates from the separation of tantalum(V) oxide were collected in volumetric flasks and diluted to a known volume. Aliquots were then taken for halide analysis.

Chloride was determined either gravimetrically as silver-(I) chloride or volumetrically by the Volhard procedure.

Bromide was determined either by titration with standard silver nitrate using eosin as the indicator or by the Volhard procedure.

#### Sulfate

Samples of the sulfate compounds were hydrolyzed in concentrated ammonia and acidified to a pH of one with 6N hydro-

chloric acid. It was necessary to add small amounts of hydrogen peroxide (one or two ml. of 30% solution) to complete the oxidation. The pure white tantalum(V) oxide was filtered off and determined as described earlier.

The filtrates from the tantalum separation were heated to near boiling and treated with a small excess of barium chloride to precipitate the sulfate as barium sulfate. This was digested over night, filtered on medium porosity filter paper, dried at  $120^{\circ}$ , ignited at  $800^{\circ}$ , and weighed as barium sulfate.

#### Oxidation-reduction titrations

The oxidation reactions for the bromide and chloride compounds were determined quantitatively by indirect titration with ammonium tetrasulfatocerate(IV) solution. Aliquots were either pipetted directly into an excess of iron(III) ammonium sulfate solution or passed through a Jones reductor into an excess of iron(III) ammonium sulfate solution. The insoluble sulfate which precipitated was filtered off and washed thoroughly with distilled water. The iron(II) in the filtrate was then titrated potentiometrically with the standard cerate solution.

## Physical Measurements

### Solution spectra

Visible and ultraviolet spectra for various solutions were obtained using a Cary Model 14 recording spectrophotometer with samples held in square, one centimeter silica cells. Freshly prepared solutions were used to insure minimum error due to air oxidation or hydrolysis of the samples.

### Infrared spectra

Infrared absorption spectra were obtained using a Perkin-Elmer, Model 21, spectrophotometer with sodium chloride optics. Samples were pressed into anhydrous potassium bromide pellets. Spectra were run for the range from 5000 to  $650\text{ cm}^{-1}$ .

### Reflectance spectra

Reflectance spectra on the various samples were obtained using a Beckman Model DU spectrophotometer with a Beckman 2580 reflectance attachment.

Samples of the polynuclear tantalum chlorides were diluted with potassium chloride while potassium bromide was used as diluent for the analogous bromides. The potassium halides were ground to pass a 200 mesh screen and dried at  $120^{\circ}$ . The same powdered potassium halide was then used as the reference material.

For convenience, the samples were packed into a stainless steel cell designed by B. A. Torp (38) for use with air sensitive samples. However, such precautions were not necessary since all samples were stable in air.

#### Conductance measurements

The conductance measurements were made using a cell which contained two square, bright platinum electrodes 2 cm. on an edge and 5 mm. apart. A Leeds and Northrup, Model 4866-60, A.C. conductance bridge was used for all measurements. The measurements were made at  $25.0 \pm 0.1^\circ$  by placing the cell in a constant temperature bath controlled to those limits.

The specific conductance for the solvent methanol was calculated by first measuring its resistance and then using Equation 5.

$$L = k(1/R) \quad (5)$$

Where:  $L$  = specific conductance in  $\text{ohm}^{-1}\text{cm.}^{-1}$ ,

$k$  = cell constant in  $\text{cm.}^{-1}$ ,

$R$  = measured resistance in ohms.

The specific conductance for a sample could then be determined by measuring the resistance of a solution of the sample, calculating the specific conductance for the solution, and subtracting the specific conductance previously determined

for the solvent.

The equivalent conductance was calculated from the specific conductance using Equation 6.

$$\Lambda = 1000(L/C) \quad (6)$$

Where:  $\Lambda$  = equivalent conductance in  $\text{cm}^2\text{eq.}^{-1}\text{ohm}^{-1}$ ,

$L$  = specific conductance in  $\text{ohm}^{-1}\text{cm.}^{-1}$ ,

$C$  = concentration in  $\text{eq. l}^{-1}$ .

#### Magnetic susceptibility measurements

Magnetic susceptibility measurements were made by Mr. J. D. Greiner, of this laboratory, using the Faraday method.

Powdered samples were packed into cylindrical Pyrex bulbs about 2 cm. long and 1 cm. in diameter. The bulbs were evacuated through a very small Pyrex tube which connected them to the vacuum line and were sealed off rapidly to avoid thermal decomposition of the sample. The weight of the sample and the weight of the bulb were determined by weighing the bulbs before and after introducing the sample and again after sealing off the bulb. Weight losses due to thermal decomposition or loss of hydrate water were held to less than three-tenths of a per cent of the sample weight.

All measurements were corrected for the diamagnetism due to the Pyrex present in the bulbs.

## Syntheses

Tantalum(V) halides

The tantalum(V) bromide and tantalum(V) chloride were prepared in good yield by direct combination of the elements as described earlier by other workers at this laboratory (1). For this procedure the reactions were carried out in a sealed Pyrex system designed so that the condensed halogen could be distilled back and forth over the metal in a central bulb of the apparatus. For the bromide the metal was maintained at 450° and for the chloride it was maintained at 400°. After reaction the excess halogen was frozen with liquid nitrogen and the product was separated in sealed bulbs. These bulbs were then opened in a dry box, maintained at a dew point of about -75°, when the tantalum(V) halides were needed for further syntheses.

Polynuclear tantalum bromide

The anhydrous dodeca- $\mu$ -bromohexatantalum dibromide was prepared by reduction of tantalum(V) bromide with aluminum metal in a two step heating process as discussed by P. J. Kuhn (1).

Twenty-six grams of tantalum(V) bromide were added to one gram of aluminum foil in a Vycor tube. The tube was

evacuated, sealed, and placed in a temperature gradient of 450 to 280° with the aluminum metal at the higher temperature. After 24 hours the tube was pulled half way out of the furnace. Excess tantalum(V) bromide and the aluminum(III) bromide formed by the reduction were sublimed out of the reaction zone at about 250° leaving a green-black solid. This material was then heated at 550° for 6 hours to produce a dark green product,  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2$ .

For subsequent procedures this dark green product was extracted with the desired solvent (water or methanol) to yield a very dark green solution characteristic of the  $\text{Ta}_6\text{Br}_{12}^{+2}$  ion and subsequently identified as such.

#### Polynuclear tantalum chloride

Anhydrous reduced chloride was prepared in exactly the same manner as the analogous bromide discussed above.

Twenty-three grams of tantalum(V) chloride were combined with 1.5 gm. of aluminum foil and heated in a gradient of 400 to 180°. Excess tantalum(V) chloride and aluminum(III) chloride were sublimed from the reaction zone at 200° and the black residue was heated at 550° for about 6 hours.

The green-brown product of this reaction is still being studied at this laboratory and remains to be positively

characterized. However, subsequent extractions of this product with water or methanol gave dark blue-green solutions definitely characteristic of the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  ion and subsequently identified as such.

Standard solutions of dodeca- $\mu$ -halohexatantalum sulfate

Standard solutions of  $(\text{Ta}_6\text{Cl}_{12})\text{SO}_4$  and  $(\text{Ta}_6\text{Br}_{12})\text{SO}_4$  were prepared by ion exchange of the original halide solutions obtained by aqueous extraction of the anhydrous reduction products.

Samples of the anhydrous reduced chloride and bromide described earlier were extracted with boiling water to yield solutions which were so green they were essentially black. The solutions were filtered away from an insoluble black residue by repeated filtrations through medium porosity filter paper. They were then passed through anion exchange resin in the sulfate form and collected in volumetric flasks with the first 50 ml. and last 50 ml. portions being discarded.

The solutions were standardized by analyzing aliquots for tantalum and halide. Ratios of halide to tantalum from 1.97 to 2.00 were obtained.



Dodeca- $\mu$ -halohexatantalum disulfates

Hydrated sulfates of the oxidized cations,  $\text{Ta}_6\text{Cl}_{12}^{+4}$  and  $\text{Ta}_6\text{Br}_{12}^{+4}$ , were prepared from solutions obtained by extracting samples of the anhydrous reduction products with boiling water and filtering as described earlier for the standard solutions. The solutions were acidified with sulfuric acid and oxidized with either their respective halogen or with  $\text{FeNH}_4(\text{SO}_4)_2$ . The chocolate-brown bromide and red-brown chloride precipitates were filtered on sintered glass, washed with ethanol and ether, and air dried.

Anal. Calcd. for  $(\text{Ta}_6\text{Br}_{12})(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ : Ta, 45.94; Br, 40.59;  $\text{SO}_4$ , 8.13. Found: Ta, 45.67; Br, 39.24;  $\text{SO}_4$ , 7.08; Br/Ta, 1.95;  $\text{SO}_4$ /Ta, 0.292.  
Calcd. for  $(\text{Ta}_6\text{Cl}_{12})(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ : Ta, 59.34; Cl, 23.26;  $\text{SO}_4$ , 10.05. Found: Ta, 59.23; Cl, 22.62;  $\text{SO}_4$ , 9.07; Cl/Ta, 1.95;  $\text{SO}_4$ /Ta, 0.288.

Dodeca- $\mu$ -bromohexatantalum tetrabromide hydrate

To prepare the bromide of the oxidized cation,  $\text{Ta}_6\text{Br}_{12}^{+4}$ , a sample of the anhydrous bromide,  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2$ , was refluxed in methanol to yield a very dark, emerald green solution. This solution was centrifuged and filtered to remove an insoluble black residue believed to be tantalum metal. The

solution was then oxidized with bromine water and acidified with 10 ml. of concentrated hydrobromic acid for every 400 ml. of solution. The solution was concentrated by boiling in air until only about 150 ml. remained. At this point a large quantity of jet black precipitate had formed and was filtered on sintered glass. The product was washed with methanol and ether and air dried.

Anal. Calcd. for  $(\text{Ta}_6\text{Br}_{12})\text{Br}_4 \cdot 5\text{H}_2\text{O}$ : Ta, 44.22;  
 Br, 52.10;  $\text{H}_2\text{O}$ , 3.67. Found: Ta, 44.30;  
 Br, 51.82;  $\text{H}_2\text{O}$  (by difference), 3.88; Br/Ta,  
 2.65;  $\text{H}_2\text{O}/\text{Ta}$ , 0.879.

Dodeca- $\mu$ -chlorohexatantalum tetrachloride hydrate

For preparation of the hydrate of the tetrachloride,  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_4$ , a sample of the anhydrous reduced chloride was dissolved in boiling water, cooled to room temperature, and filtered three times through medium porosity paper to separate an insoluble black residue. The resulting very dark, blue-green solution was made 3N with hydrochloric acid and oxidized by bubbling chlorine gas through the solution. A red-brown precipitate formed immediately and was allowed to settle. The product was filtered on sintered glass, washed with water, and air dried.

Anal. Calcd. for  $\text{Ta}_6\text{Cl}_{16} \cdot 9\text{H}_2\text{O}$ : Ta, 59.80; Cl, 31.26;  
 $\text{H}_2\text{O}$ , 8.93. Found: Ta, 59.95; Cl, 31.01;  $\text{H}_2\text{O}$   
 (by difference), 9.04; Cl/Ta, 2.64;  $\text{H}_2\text{O}/\text{Ta}$ , 1.51.

Dodeca- $\mu$ -chlorohexatantalum dichloride hydrate

The hydrated dichloride,  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ , was prepared by dissolving a quantity of the anhydrous reduced chloride in boiling water to yield a dark blue-green solution. The solution was allowed to cool to room temperature and filtered three times through medium porosity filter paper. The filtered solution was made just acidic to pH paper and refiltered. It was then evaporated to dryness on the vacuum line and pumped under continuous vacuum for 12 hours after the last trace of solvent was removed.

Anal. Calcd. for  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ : Ta, 61.60;  
 Cl, 28.18;  $\text{H}_2\text{O}$ , 10.22. Found: Ta, 61.47;  
 Cl, 28.25;  $\text{H}_2\text{O}$  (by difference), 10.28;  
 Cl/Ta, 2.34;  $\text{H}_2\text{O}/\text{Ta}$ , 1.68.

Dodeca- $\mu$ -bromohexatantalum dibromide hydrate

The hydrated dibromide,  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2 \cdot 8\text{H}_2\text{O}$ , was prepared by dissolving a sample of the anhydrous bromide,  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2$ , in boiling water to yield a dark emerald green solution. The solution was cooled to room temperature and filtered three

times through medium porosity filter paper. It was then evaporated to dryness on the vacuum line and pumped under continuous vacuum for 12 hours.

Anal. Calcd. for  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2 \cdot 8\text{H}_2\text{O}$ : Ta, 46.21;  
Br, 47.64;  $\text{H}_2\text{O}$ , 6.14. Found: Ta, 45.99;  
Br, 47.98;  $\text{H}_2\text{O}$  (by difference), 6.03; Br/Ta,  
2.36;  $\text{H}_2\text{O}/\text{Ta}$ , 1.32.

The compound  $\text{Ta}_6\text{Cl}_{17} \cdot x\text{H}_2\text{O}$

A compound with the apparent composition  $\text{Ta}_6\text{Cl}_{17} \cdot 8\text{H}_2\text{O}$  was prepared by refluxing a sample of the anhydrous reduced chloride with methanol for 6 hours to obtain a dark blue-green solution. This solution was centrifuged and filtered to separate it from an insoluble black residue. It was then oxidized with chlorine gas, acidified with concentrated hydrochloric acid (10 ml. to 400 ml. of solution) and concentrated to a small volume by boiling in air. The red sparkling precipitate which formed was filtered on sintered glass and air dried.

Anal. Calcd. for  $\text{Ta}_6\text{Cl}_{17} \cdot 8.5\text{H}_2\text{O}$ : Ta, 58.94; Cl, 32.74;  
 $\text{H}_2\text{O}$ , 8.32. Found: Ta, 58.89; Cl, 32.74;  $\text{H}_2\text{O}$   
(by difference), 8.37; Cl/Ta, 2.84;  $\text{H}_2\text{O}/\text{Ta}$ ,  
1.43.

## RESULTS AND DISCUSSION

Preparation of Crystalline Salts of the  $\text{Ta}_6\text{X}_{12}^{+2}$  Ions

With the exception of a report of magnetic susceptibilities by Krylov (37) and extinction coefficients by Kuhn (1), no quantitative physical measurements have been given in the literature for crystalline salts of the polynuclear tantalum halide ions.

In an attempt to prepare such a crystalline salt, a number of reagents were added to solutions of  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2$  in water. Solutions of carbonate, phosphate, hexacyanoferrate(II), tetrachlorostannate(II), sulfate, perchlorate, fluoride, nitrate, oxalate and tetraphenylborate(III) with the  $\text{Ta}_6\text{Br}_{12}^{+2}$  ion were prepared. Only oxalate and tetraphenylborate(III) produced crystalline precipitates with no apparent decomposition in the green solutions.

The precipitation with oxalate left the solution nearly colorless, indicating almost quantitative formation of the product. The salt was dark green, almost black, and obviously crystalline. Under 10X magnification the crystals appeared as thin rhombohedral plates which were transparent green when oriented face up.

The tetraphenylborate(III) precipitation was likewise nearly quantitative and yielded a dark green, nearly black, crystalline product. Under 40X magnification the black crystals appeared to be nearly perfect octahedra.

The tetraphenylborate salt was readily soluble in tetrahydrofuran, 2,4-pentanedione, acetonitrile, ethanol, and ether. It was completely insoluble in petroleum ether, carbon tetrachloride and chloroform. However, it proved to be too unstable for further use. On standing for short periods of time the odor of benzene could be detected above the sample, indicating a decomposition of the tetraphenylborate group. Analysis of the tetraphenylborate salt was unsatisfactory but gave a ratio of tetraphenylborate to tantalum of 0.29 which approaches the value of 0.33 expected for  $(\text{Ta}_6\text{Br}_{12})(\text{Ph}_4\text{B})_2$ .

In order to obtain compounds suitable for magnetic susceptibility measurements, it was necessary to prepare the hydrated halides. The preparation of  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2 \cdot 10\text{H}_2\text{O}$  was relatively straightforward, requiring only the evaporation in vacuo of a slightly acid solution of the halide to obtain the crystalline salt. The presence of a slight excess of hydrochloric acid was considered necessary to inhibit

hydrolysis of the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  ion in the solution. The product was dark green and dissolved slowly in water to give the characteristic blue-green color of the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  ion in aqueous solution.

The analogous bromide proved to be somewhat more difficult to prepare. Attempts to crystallize the salt by evaporation of solutions acidified with hydrobromic acid yielded products with a large excess of bromide present. Subsequent investigations indicated that the  $\text{Ta}_6\text{Br}_{12}^{+2}$  ion was precipitated from aqueous solution by an excess of hydrobromic acid. However, the pure compound  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2 \cdot 8\text{H}_2\text{O}$  was finally obtained by evaporation in vacuo of a solution of the  $\text{Ta}_6\text{Br}_{12}^{+2}$  ion with no hydrobromic acid added. The product was dark green and dissolved rapidly in water to give a solution with the characteristic emerald green color.

It should be stated here that the hydrate numbers as determined by difference for these products are accurate only within the limits of  $\pm 1$  mole of water per mole of compound. Differences as small as one per cent in the total analysis for tantalum and halide were sufficient to change the hydrate number by one unit. For that reason, this limit of error in the value of hydrate numbers applies throughout this work.

The formulation of the dihalides as seven hydrates by Chapin (3) was based on an actual analysis for water, but values reported by Kuhn (1) apparently are accurate to the same limits reported here.

#### Oxidation Titrations and the Dodeca- $\mu$ -halohexatantalum Disulfates

Preliminary investigations of a solution of  $\text{Ta}_6\text{Br}_{12}^{+2}$  had indicated a color change from green to pale orange when cerium(IV) was added. A quantitative study of this oxidation reaction was then initiated.

Solutions prepared by direct dissolution of the anhydrous products were difficult to standardize. Excess halide ion was always present due to hydrolysis of various contaminants in the anhydrous materials. To be absolutely sure the halogen to tantalum ratio was 2:1 for the complex cation in solution, it was necessary to eliminate the ionized halide. This was accomplished by exchanging the halide for another anion using an exchange resin. Ionized halide was exchanged for nitrate, perchlorate or sulfate.

Solutions exchanged for nitrate were unstable with respect to oxidation of the  $\text{Ta}_6\text{X}_{12}^{+2}$  by nitrate ion. Even



in stoppered flasks the solutions rapidly changed in color from green to brown indicating partial oxidation had taken place. Later it became necessary to pass some solutions through a Jones reductor, and nitrate ion is rapidly reduced by amalgamated zinc in an acid solution making a quantitative titration impossible.

Dilute perchlorate solution was apparently stable at room temperature. However, when concentrated slowly on a hot plate, a sample of the solution detonated. In the absence of more knowledge concerning this violent reaction, no further work was done with the perchlorates.

Sulfate solutions were thus chosen for the quantitative cerium titrations. Attempts to titrate the  $\text{Ta}_6\text{X}_{12}\text{SO}_4$  solutions directly were uniformly unsuccessful. The oxidation was accompanied by formation of a brown precipitate which formed an impervious coat on the platinum electrode producing erratic results. Therefore, an indirect method using iron(III) ammonium sulfate in dilute sulfuric acid as the oxidant, was utilized. The brown precipitate still complicated the titration and was removed by filtration before titrating the iron(II) with cerium(IV). It was found that the filtrates from the separation of the brown precipitate contained

no halide, indicating the basic  $Ta_6X_{12}$  unit had remained intact during the oxidation with iron(III) and was contained in the precipitate. Table 2 summarized the titration results.

Table 2. Results of the oxidation titrations of the  $Ta_6X_{12}SO_4$  solutions

Sample	Stirring time with iron(III) solution	Iron(II) found, meq.	Tantalum present, meq.	Ratio found, Fe/6Ta
Bromide <sup>a</sup>	5 hrs.	0.09535	0.2706	2.11
Bromide <sup>a</sup>	30 min.	0.09535	0.2706	2.01
Bromide	4.5 hrs.	0.3000	0.9039	1.99
Bromide <sup>b</sup>	30 min.	0.3170	1.002	1.89
Bromide <sup>a,b</sup>	30 min.	0.3289	1.002	1.97
Chloride <sup>b</sup>	30 min.	0.2431	0.8038	1.81
Chloride <sup>a,b</sup>	30 min.	0.2717	0.8038	2.03

<sup>a</sup>Solutions which were passed through a Jones reductor.

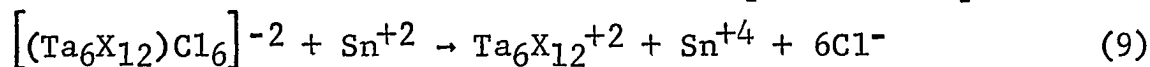
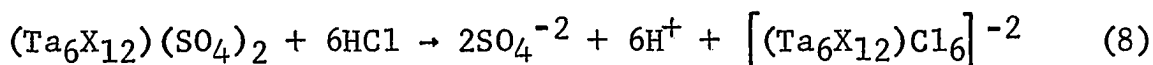
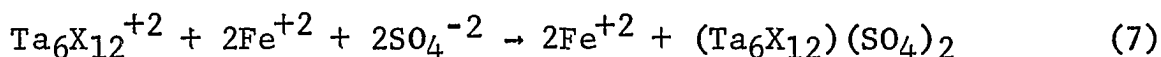
<sup>b</sup>Solutions which were about one week old.

It is apparent that the  $Ta_6X_{12}^{+2}$  ions underwent a two electron oxidation on reaction with iron(III). The results were independent of stirring time with the iron(III) ammonium sulfate but were apparently influenced by the age of the solutions. The last four titrations listed in Table 2 illustrate this aging effect and show that full reducing power could be restored by passing the solutions through a Jones reductor.

The observation that no halide was liberated in the oxidation process, coupled with the fact that a precipitate had formed when the oxidation was carried out in the presence of sulfate, suggested that the precipitate was an insoluble disulfate of the oxidized cation. Samples of the bromide and chloride disulfates were prepared by oxidation of sulfate solutions with bromine or with iron(III) ammonium sulfate. Analytical results for the products and the calculated values for the expected compounds were given in the Experimental section of this work. The analyses were not exactly in agreement with calculated values but indicated that the products were indeed  $(\text{Ta}_6\text{Cl}_{12})(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$  and  $(\text{Ta}_6\text{Br}_{12})(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$  as expected. Here again the hydrate numbers are accurate to only  $\pm 1$  mole of water per mole of compound as discussed earlier for the dihalide derivatives.

The compounds were insoluble in water, alcohol, and ether but dissolved slowly in boiling hydrochloric acid-methanol mixtures giving orange-red solutions. Because the presence of hydrochloric acid was required before the products would dissolve in methanol, it was assumed that dissolution was accomplished by formation of complex anions such as  $[(\text{Ta}_6\text{X}_{12})\text{Cl}_6]^{-2}$ . Proof that the original  $\text{Ta}_6\text{X}_{12}$  unit had

remained intact during the oxidation process was provided by the observation that the acidic alcohol solutions could be reduced by tin(II) chloride or zinc amalgam back to the green color characteristic of the  $\text{Ta}_6\text{X}_{12}^{+2}$  ions. The cyclic oxidation-solution-reduction scheme observed for both the  $\text{Ta}_6\text{Cl}_{12}$  and  $\text{Ta}_6\text{Br}_{12}$  groups can be summarized as shown in Equations 7, 8 and 9.



#### Dodeca- $\mu$ -halohexatantalum Tetrahalides

Identification of the oxidized sulfates prompted a search for other compounds containing the oxidized  $\text{Ta}_6\text{X}_{12}$  unit. Because hydrolysis seemed to be a likely source of contamination, the initial studies were carried out in methanol, where solvolysis reactions should be less serious.

Solutions of the reduced chloride in methanol were oxidized with chlorine, treated with tetramethylammonium chloride, and evaporated to a small volume in an attempt to prepare the  $(\text{Me}_4\text{N})_2[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6]$  salt. This would be analogous to the molybdenum compounds reported by Sheldon (20).

However, the product gave an infrared absorption spectrum which did not contain bands characteristic of the C-H stretching modes in the tetramethylammonium ion. Analysis indicated a halogen to tantalum ratio much too low for the  $[(Ta_6Cl_{12})Cl_6]^{-2}$  ion. A discussion of the product finally isolated from acidic methanol solutions will be presented later.

Subsequently, a solution of the reduced bromide was oxidized with bromine water, acidified with hydrobromic acid and evaporated to yield a black crystalline product identified by analysis as  $(Ta_6Br_{12})Br_4 \cdot 5H_2O$ . The product was insoluble in water, pure methanol, and ether. Methanol acidified with hydrochloric acid dissolved it slowly to yield an orange-red solution, and wet methanol apparently reduced it yielding a green solution characteristic of the  $Ta_6Br_{12}^{+2}$  ion. Samples of the product added to hot ammonia solution were rapidly reduced to the green  $Ta_6Br_{12}^{+2}$  and then converted, on further heating, to a brown insoluble product. The brown product was rapidly oxidized to the tantalum(V) oxide by dilute nitric acid. This reaction sequence formed the basis for the analytical procedure utilized for the tetrabromide.

As explained earlier the alcoholic preparation procedure

applied to the reduced chloride did not produce the expected tetramethylammonium salt or, apparently, the simpler  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_4$  compound. A study of the oxidation of the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  ion in various concentrations of aqueous hydrochloric acid had indicated the nearly quantitative precipitation of a red-brown product with acid concentrations of two normal or greater. Below two normal in acid, the solutions remained orange-red and gave absorption spectra with maxima at 340 and 415  $\text{m}\mu$ . Neutral solutions apparently gave a different product on oxidation. They were paler in color and gave absorption spectra with a single maximum at 318  $\text{m}\mu$  which faded rapidly leaving the solution clear and colorless.

Oxidation of a concentrated solution of the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  ion in 3N hydrochloric acid gave a large quantity of the red-brown product which was identified as  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_4 \cdot 9\text{H}_2\text{O}$  by analysis. This compound was slightly soluble in water and acidic methanol but was reduced in boiling wet methanol to give a solution with the blue-green color characteristic of the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  ion. As with the analogous bromide compound, the tetrachloride was reduced by boiling ammonia solution. However, in contrast to the bromide, concentrated nitric acid or hydrogen peroxide was required for complete oxidation to

tantalum(V).

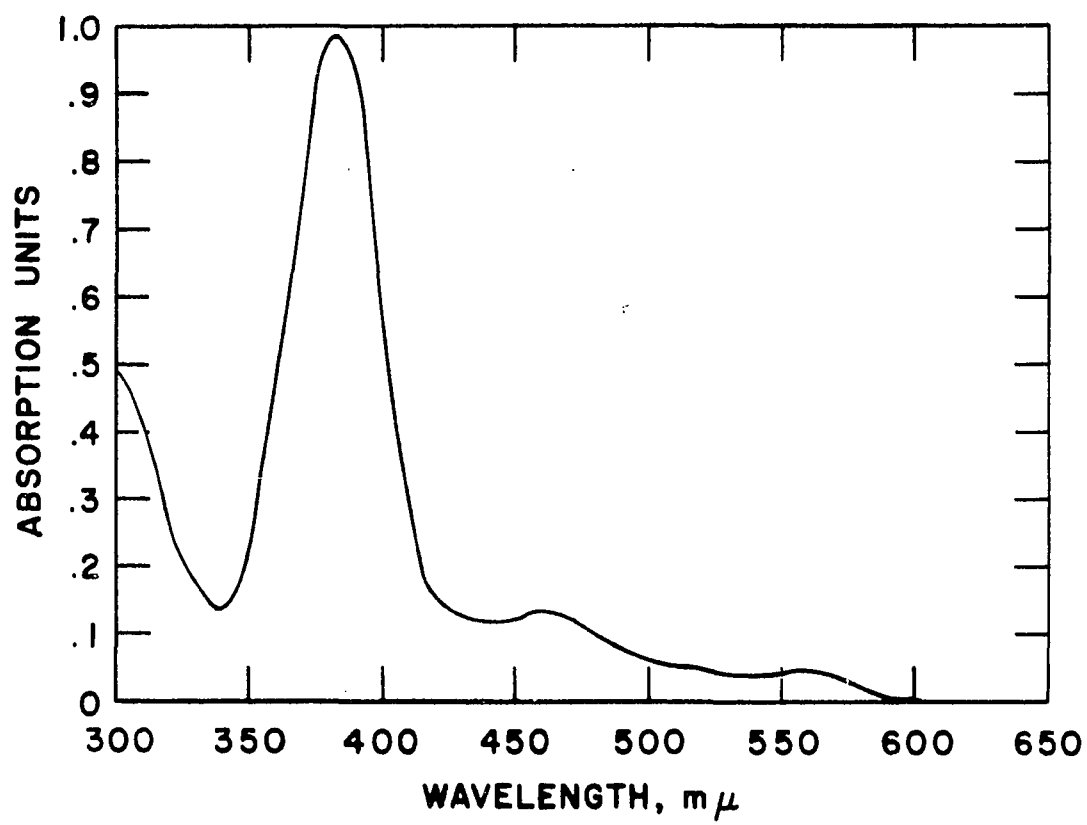
The lack of solubility of the tetrahalides in available solvents precluded the determination of molecular weights and extinction coefficients. Figure 2 shows the spectra obtained for the tetrabromide in methanol-hydrochloric acid solution. Comparison with reflectance spectra for the solid tetrabromide, shown in Figure 8, reveals a strong correlation. The very intense, symmetrical peak at 383  $m\mu$  was found again in the reflectance spectra as the most intense absorption at 385  $m\mu$ . Shoulders at ca. 455  $m\mu$  in the solution and ca. 445  $m\mu$  in the solid also correlate with poor resolution making exact location of these peaks difficult. The form of the  $Ta_6Br_{12}^{+4}$  ion in the acidic methanol solution was unknown. However, as discussed for the disulfates, the presence of hydrochloric acid was necessary to effect the dissolution of the tetrabromide and the formation of a complex anion in solution seems likely.

#### The Polynuclear Tantalum Chloro-acid

As indicated earlier the oxidation of the  $Ta_6Cl_{12}^{+2}$  ion in methanol-hydrochloric acid solutions gave a product which was distinctly different from the tetrahalides. The product

Figure 2. Absorption spectrum for  $(\text{Ta}_6\text{Br}_{12})\text{Br}_4$   
in hydrochloric acid-methanol solution





was obtained as sparkling red crystals which appeared to be roughly octahedral in shape when viewed under high magnification. The material was readily soluble to give an orange-red solution in oxygen-solvents such as acetone, alcohol, tetrahydrofuran, glacial acetic acid, and ether but was insoluble in water. It dissolved in concentrated sulfuric acid with evolution of some hydrogen chloride. The resulting orange-red solution was stable even when heated until fumes of  $\text{SO}_3$  were evolved.

Analysis of the product gave the formula  $\text{Ta}_6\text{Cl}_{17} \cdot \text{XH}_2\text{O}$  with a variable number of waters as determined by difference. Chloride to tantalum ratios gave extremes of 2.80 and 2.86, but most preparations gave products with ratios very close to the calculated value of 2.833. No change in this ratio was observed when the compound was recrystallized from acidic methanol.

It was felt that this compound did not actually represent a new oxidation state for the  $\text{Ta}_6\text{Cl}_{12}$  unit. If this unit was present as  $\text{Ta}_6\text{Cl}_{12}^{+4}$ , the compound would have to contain a complex anion of the type  $\left[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_{4+n}\right]^{-n}$ . To confirm this, samples of the compound were dissolved in 50% methanol-water solution and passed through anion and cation

exchange resins. As expected the orange-red color passed directly through the cation exchange resin but was completely removed from the solution by the anion exchange resin. Further proof of this anionic state was provided by the observation that silver(I) ion precipitated the color from methanol solutions of the compound as a red-brown solid. Attempts to analyze the silver precipitation product were unsuccessful.

It thus appeared that the compound was the hydronium salt of a complex chloroanion and should act as a strong acid in solution. A determination of the conductivity for a  $1.63 \times 10^{-4}$  molar solution of the compound gave a value of  $201 \text{ cm}^2 \text{ mole}^{-1} \text{ ohm}^{-1}$ . Such a high conductivity should be expected for a compound yielding hydrogen ion on dissolution. Furthermore, pH titrations of the material in 90% methanol-water solution with standard sodium hydroxide produced titration curves with large breaks at the equivalence point. Values for the number of equivalents of hydroxide consumed per mole of compound ranged from 1.75 to 1.87.

Because it was believed that these nonintegral values were due to contamination by insoluble impurities, a sample of the product was dissolved in absolute methanol, filtered, and diluted to 250 ml. 50 ml. aliquots of this solution were

analyzed and found to contain 1.011 meq. of tantalum. Duplicate aliquots were then titrated with standard sodium hydroxide and found to require 0.3282 meq. of base. This produced a ratio of 1.95 equivalents of base consumed for every six equivalents of tantalum and supported the assumption that the product was a dibasic acid such as  $(\text{H}_3\text{O})_2[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_6] \cdot x\text{H}_2\text{O}$  contaminated with insoluble impurities.

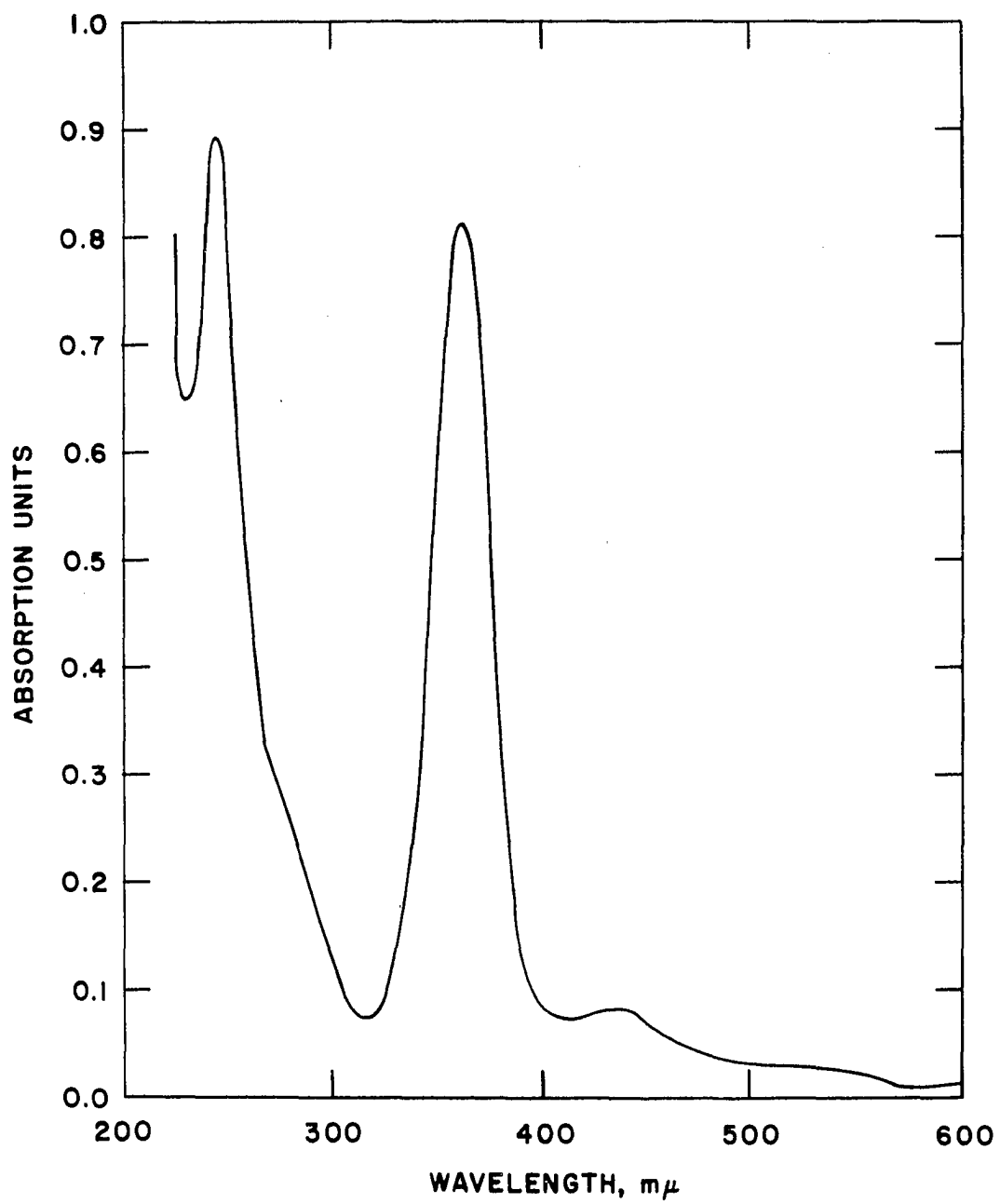
Infrared, visible and ultraviolet spectra were obtained for this acid. The infrared spectra contained bands at 3420 and 1630  $\text{cm}^{-1}$  which represent, respectively, the O-H stretching and O-H bending modes for lattice water (39, p. 156). Figure 3 illustrates the visible and ultraviolet spectra for the product in absolute methanol solution. Because of the serious contamination of the product and difficulties encountered in purification procedures, no further studies on the compound were carried out.

## Spectra

### Infrared spectra

With the exception of the two disulfates and the tetrabromide, the infrared absorption spectra for all of the hydrated polynuclear compounds contained only two bands.

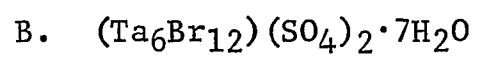
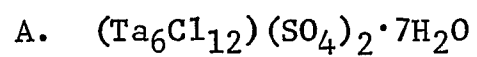
Figure 3. Absorption spectrum for a  $1.63 \times 10^{-4}$   
molar solution of  $\text{Ta}_6\text{Cl}_{17}$  in methanol



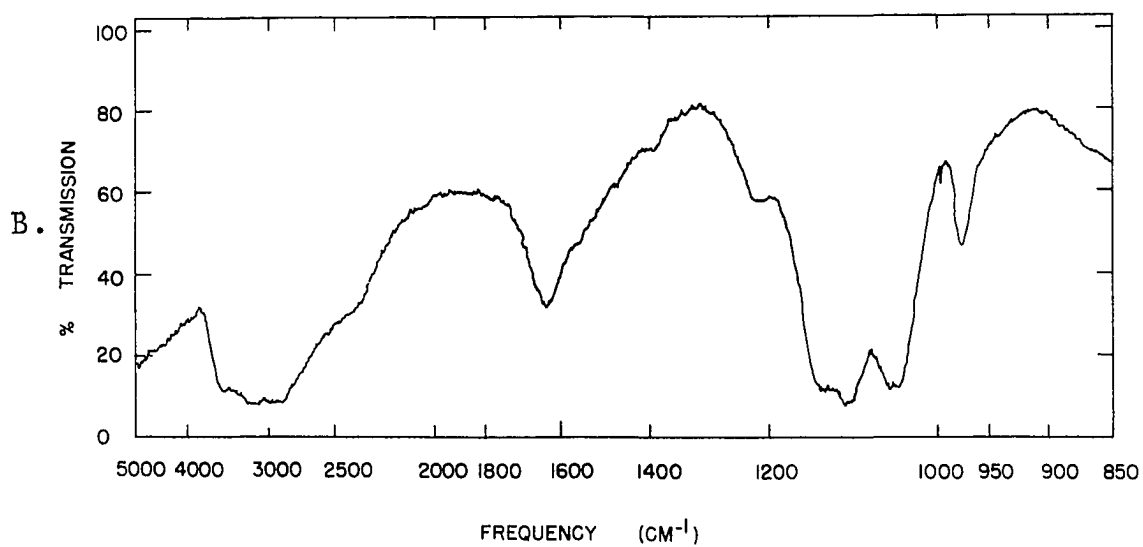
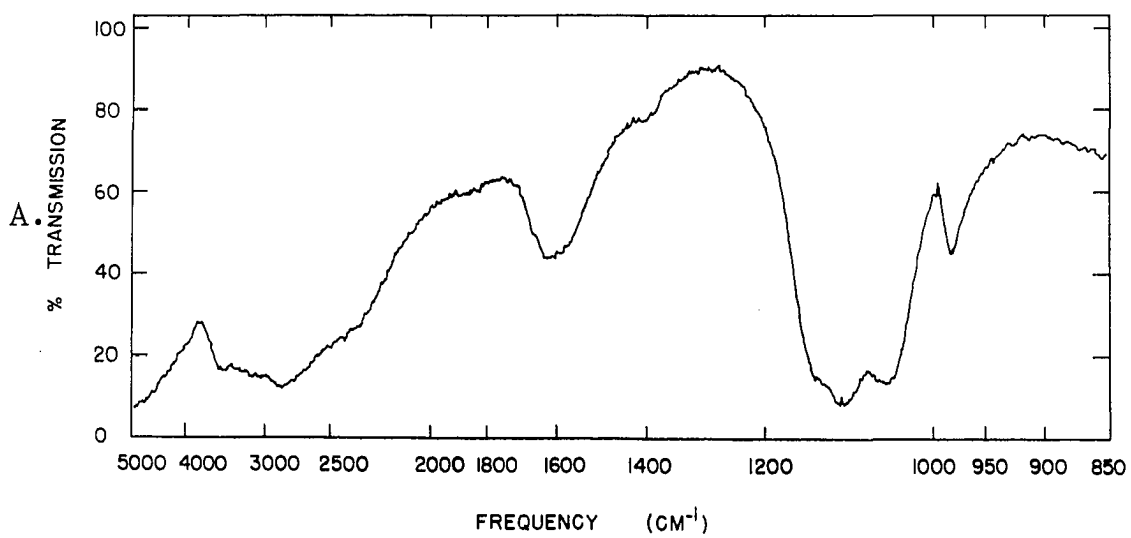
These bands occurred at about  $3500\text{ cm.}^{-1}$  and at  $1630\text{ cm.}^{-1}$  and can be assigned to the O-H stretching and O-H bending modes for lattice water (39, p. 156).

The infrared absorption spectra for the dodeca- $\mu$ -chlorohexatantalum disulfate and the dodeca- $\mu$ -bromohexatantalum disulfate are shown in Figure 4. In addition to the two bands already mentioned as being characteristic of lattice water, these spectra contained bands arising from the symmetric ( $\nu_1$ ) and antisymmetric ( $\nu_3$ ) S-O stretching modes in the sulfate group. According to Nakamoto (39, p. 164) the appearance of the  $\nu_1$  band and the splitting of the  $\nu_3$  band are strong evidence for coordination of the sulfate group. Lowering of the symmetry through coordination makes the  $\nu_1$  symmetric stretching mode infrared active and splits the ordinarily degenerate  $\nu_3$  mode into two or more bands. For these compounds,  $\nu_1$  appears at  $980\text{ cm.}^{-1}$  for the chloride and at  $975\text{ cm.}^{-1}$  for the bromide. The  $\nu_3$  band is split into bands at 1045, 1100, and 1125  $\text{cm.}^{-1}$  for the bromide and at 1045 and 1100  $\text{cm.}^{-1}$  for the chloride. Thus, it appears that the sulfate group in these compounds is bonded directly to the  $\text{Ta}_6\text{X}_{12}$  unit.

Figure 4. Infrared absorption spectra for the dodeca- $\mu$ -halohexatantalum disulfates







The infrared absorption spectra for the dodeca- $\mu$ -bromohexatantalum tetrabromide hydrate contained the bands characteristic of lattice water and, in addition, contained a third band at  $990\text{ cm.}^{-1}$ . To confirm that this band was also associated with water, a sample of the compound was prepared from a methanol solution to which deuterium had been added as  $\text{D}_2\text{O}$ . In the spectrum for the deuterated compound, all of the bands had been split including the one originally observed at  $990\text{ cm.}^{-1}$ . Table 3 lists the absorption maxima found for the two compounds and their assignments.

Table 3. Infrared absorption bands observed for the deuterated and undeuterated dodeca- $\mu$ -bromohexatantalum tetrabromide

Sample	$\nu$ , $\text{cm.}^{-1}$	Assignment
Undeuterated	3500	O-H stretching
	1630	O-H bending
	990	H-O-H rocking
Deuterated	$\sim 3500$ (broadened)	O-H, O-D stretching
	1575	O-H bending
	1330	O-D bending
	1050	O-H rocking
	782	O-D rocking

Nakamoto (39, p. 156) indicates that infrared activation of the H-O-H rocking mode for water is characteristic of coordination. Thus it appears that water is bound directly

to the  $\text{Ta}_6\text{Br}_{12}$  unit in the dodeca- $\mu$ -bromohexatantalum tetrabromide hydrate. Figure 5 shows the infrared spectra obtained for the tetrabromide with the analogous tetrachloride included for comparison.

#### Visible and ultraviolet solution spectra

Spectra and extinction coefficients were obtained for aqueous solutions of the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  and  $\text{Ta}_6\text{Br}_{12}^{+2}$  ions and are shown in Figure 6. The apparent extinction coefficients for the major peaks are given in Tables 4 and 5.

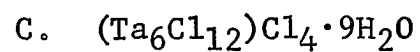
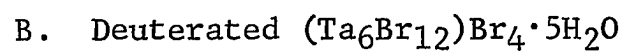
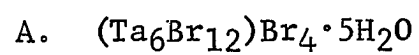
Table 4. Apparent extinction coefficients for absorption maxima in the aqueous solution spectra of  $\text{Ta}_6\text{Br}_{12}^{+2}$

$\lambda$ , m $\mu$	$\nu$ , $\text{cm}^{-1} \times 10^{-4}$	$\epsilon$ , $\ell \text{ mole}^{-1} \text{cm}^{-1}$
748	1.34	3,790
639	1.56	5,760
500	2.00	1,160
421	2.37	3,600
352	2.84	14,670

Table 5. Apparent extinction coefficients for absorption maxima in the aqueous solution spectra of  $\text{Ta}_6\text{Cl}_{12}^{+2}$

$\lambda$ , m $\mu$	$\nu$ , $\text{cm}^{-1} \times 10^{-4}$	$\epsilon$ , $\ell \text{ mole}^{-1} \text{cm}^{-1}$
750	1.33	3,140
638	1.56	5,360
472	2.12	1,050
398	2.51	3,430
330	3.03	19,270
284	3.52	6,380

Figure 5. Infrared absorption spectra for the dodeca- $\mu$ -halohexatantalum tetrahalides



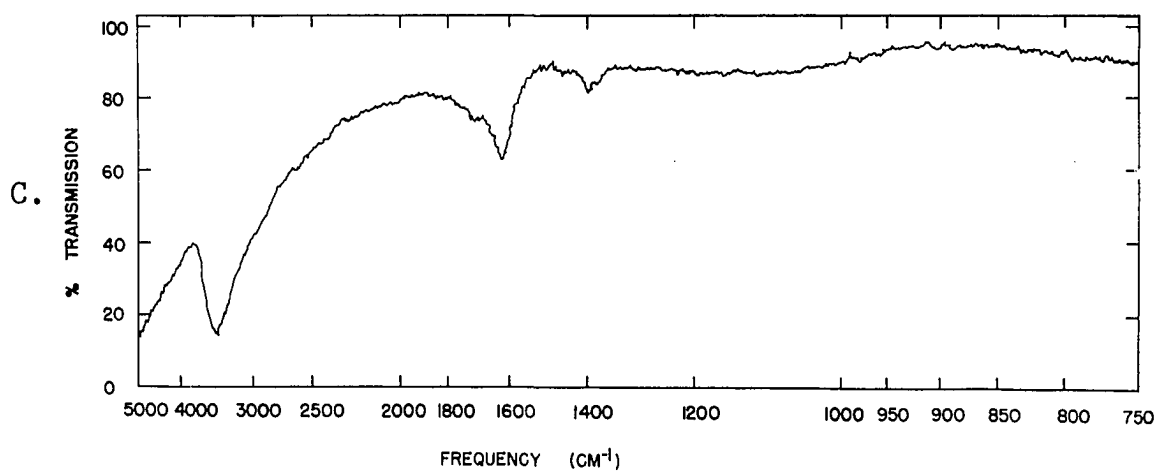
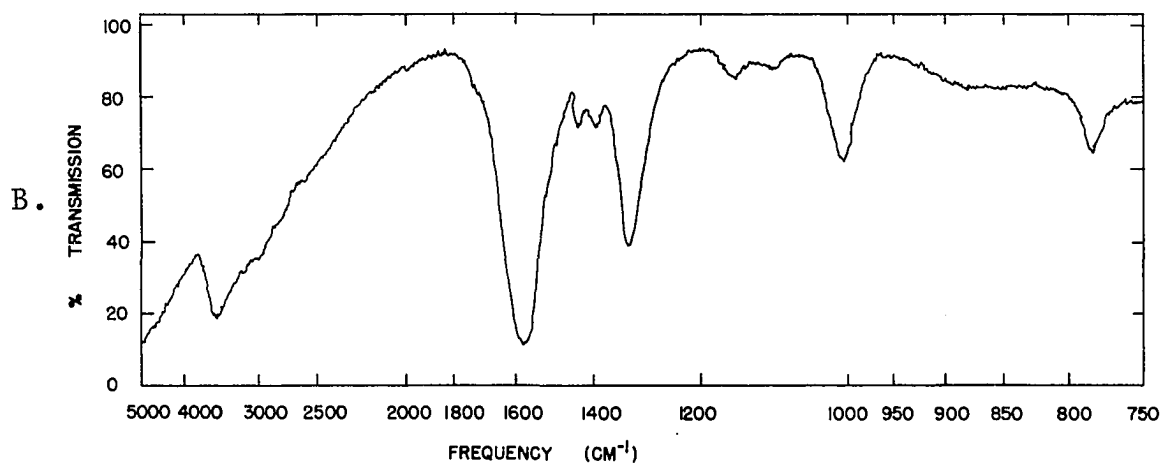
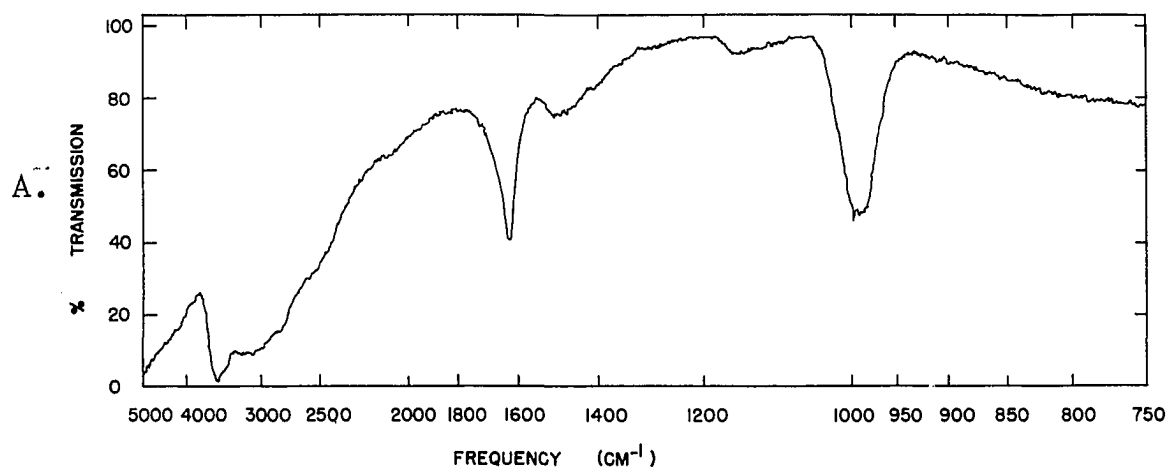
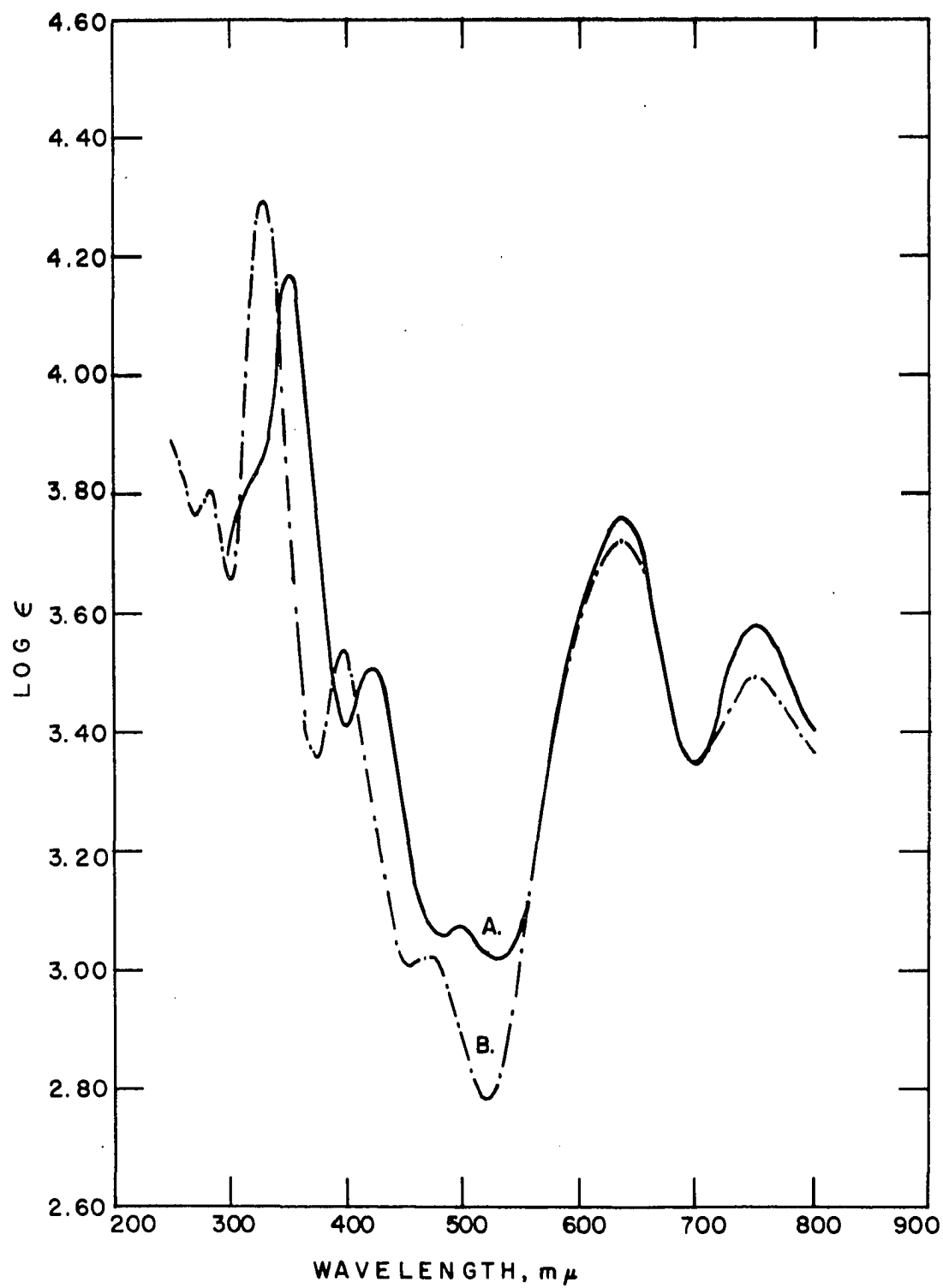


Figure 6. Visible and ultraviolet absorption spectra  
for the reduced polynuclear tantalum halides  
in aqueous solution

A.  $\text{Ta}_6\text{Br}_{12}^{+2}$  (solid line)

B.  $\text{Ta}_6\text{Cl}_{12}^{+2}$  (broken line)



The most striking feature of these two spectra is their marked similarity. The absorption maxima found at the red end of the visible portion of the spectrum are essentially identical. They must arise from transitions between levels of exactly the same energy for the chloride and the bromide. The presence of levels with the exact same energy values in two related compounds is extremely unusual. Such levels must be closely associated with bonding in the octahedron of metal atoms which make up the core of both compounds and must be essentially free of contributions from halogen bonding. Further evidence that the bands at the red end of the spectrum arise from transitions between levels devoid of halogen character is provided by the spectrum of  $\text{Ta}_6\text{I}_{12}^{+2}$  (1). Bands in the spectrum of  $\text{Ta}_6\text{I}_{12}^{+2}$  were found at 750 and 635  $\text{m}\mu$ . The three maxima which occur at the ultraviolet end of the spectra for  $\text{Ta}_6\text{Cl}_{12}^{+2}$  and  $\text{Ta}_6\text{Br}_{12}^{+2}$  are also quite similar. A difference of only 30  $\text{m}\mu$  separates these maxima for the bromide and chloride. They apparently arise from transitions between levels more involved with halogen bonding in the  $\text{Ta}_6\text{X}_{12}$  unit.

#### Reflectance spectra

The reflectance spectra obtained for  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_4 \cdot 9\text{H}_2\text{O}$

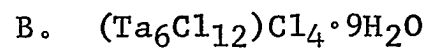
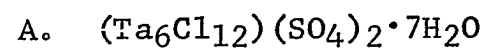


and  $(\text{Ta}_6\text{Cl}_{12})(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$  are shown in Figure 7, and those obtained for  $(\text{Ta}_6\text{Br}_{12})\text{Br}_4 \cdot 5\text{H}_2\text{O}$  and  $(\text{Ta}_6\text{Br}_{12})(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$  are shown in Figure 8. Actual dilution values for the powdered mixtures were not known.

The oxidized chloride derivatives yield spectra which are nearly identical. Absorption maxima were found at 925, 755, 495, 415, 345, 285, and 235  $\text{m}\mu$  for the tetrachloride and at 925, 775, 495, 420, 345, 280, and 225  $\text{m}\mu$  for the disulfate. Because of the poor resolution obtained with reflectance spectra, these assignments are only approximate for all but the most intense peaks at 345  $\text{m}\mu$ . The peak at 925  $\text{m}\mu$  was particularly hard to distinguish, for its presence was indicated in both spectra only as a shoulder on the more intense band at ca. 775  $\text{m}\mu$ .

The spectra obtained for the oxidized bromide derivatives were less similar than those obtained for the chlorides. Absorption maxima were found at 875, 740, 530, 445, 385, 295, and 260  $\text{m}\mu$  for the tetrabromide and 845, 720, 530, 435, 265, 287, and 247  $\text{m}\mu$  for the disulfate. Again poor resolution prevents more than approximate location of these peaks. The lesser similarity between spectra for the bromide derivatives may be explained in part by considering the evidence pre-

Figure 7. Visible and ultraviolet reflectance spectra for dodeca- $\mu$ -chlorohexatantalum disulfate and tetrachloride



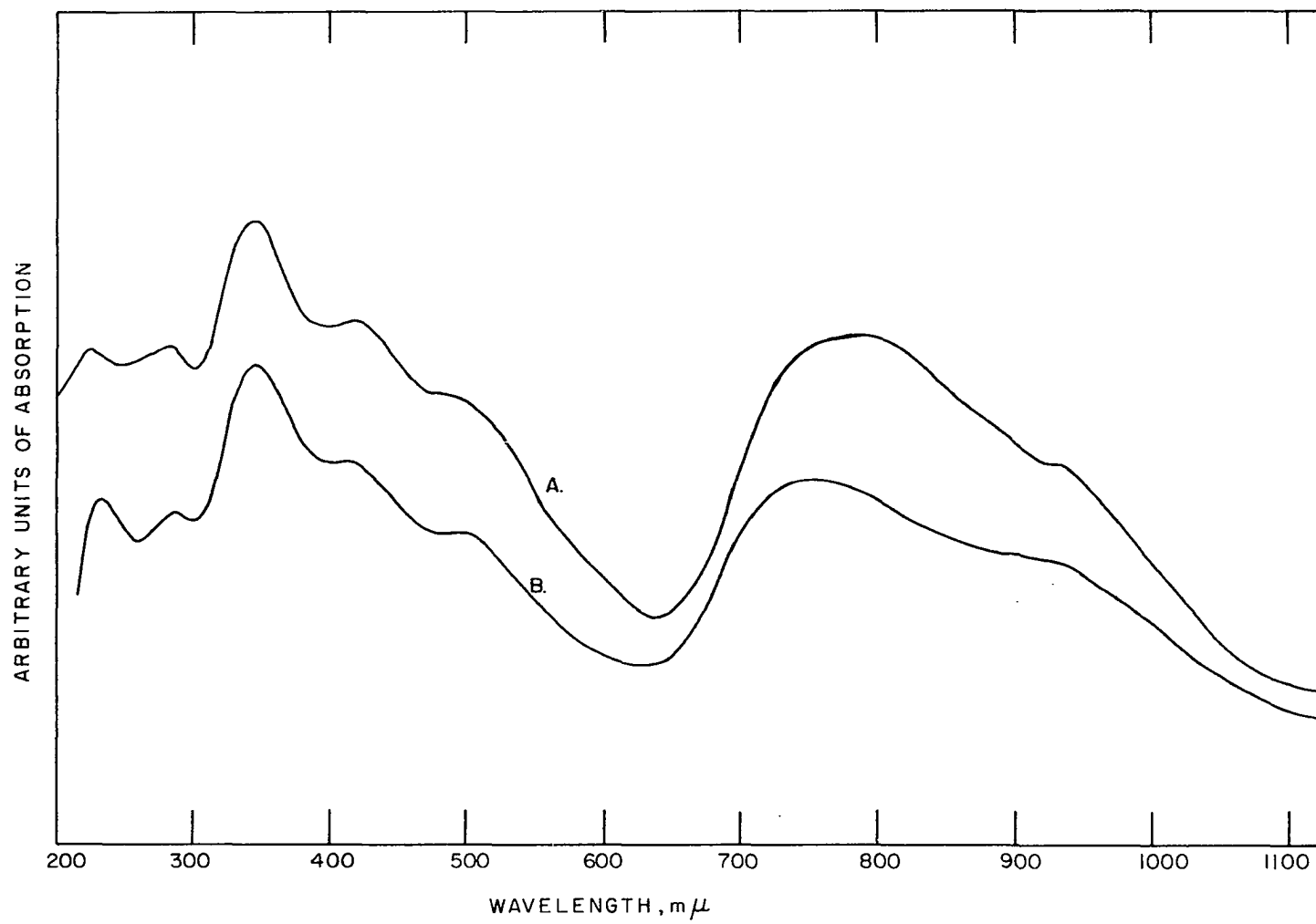
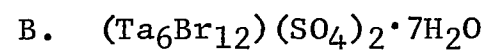
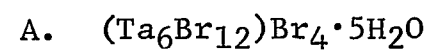
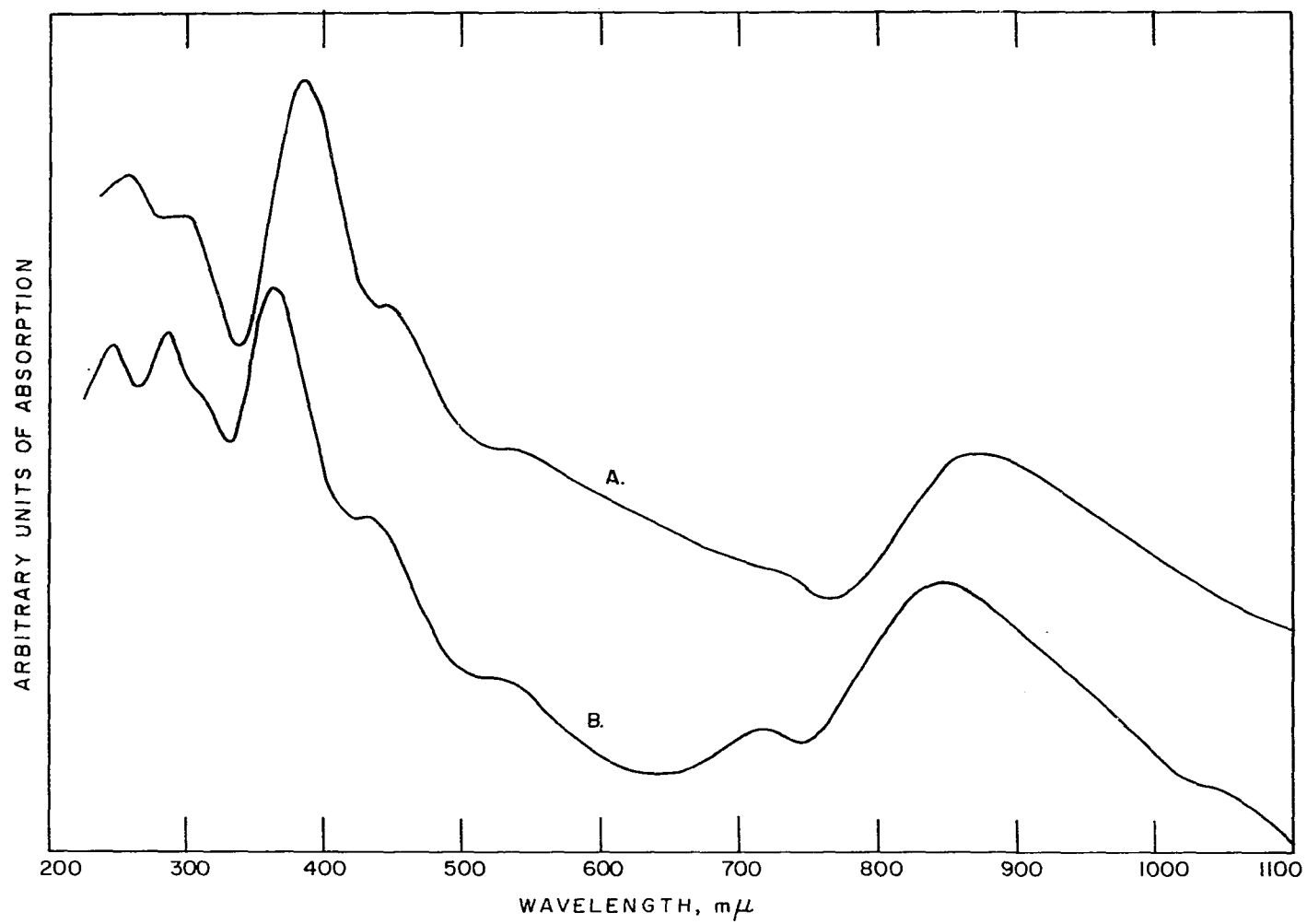


Figure 8. Visible and ultraviolet reflectance spectra for dodeca- $\mu$ -bromohexatantalum tetrabromide and disulfate





sented by infrared data. As discussed earlier, the dodeca- $\mu$ -bromohexatantalum tetrabromide is apparently the only compound found to definitely contain water bonded as a ligand to the polynuclear core. This could conceivably cause slight variations in symmetry which in turn would shift the observed absorption maxima by small amounts.

#### Summary of observations on spectra

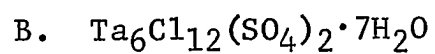
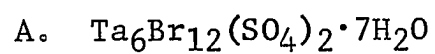
Results obtained from these studies indicate a strong similarity in the spectra of the compounds, whether oxidized or reduced, bromide or chloride. All contain three absorption maxima at the edge of the ultraviolet region of the spectrum with the same stair-step relative intensities. The position of the strongest of these absorptions varies only about 50 m $\mu$  over the entire range of compounds studied. This grouping of three peaks must be quite characteristic of the Ta<sub>6</sub>X<sub>12</sub> core structure present in each compound.

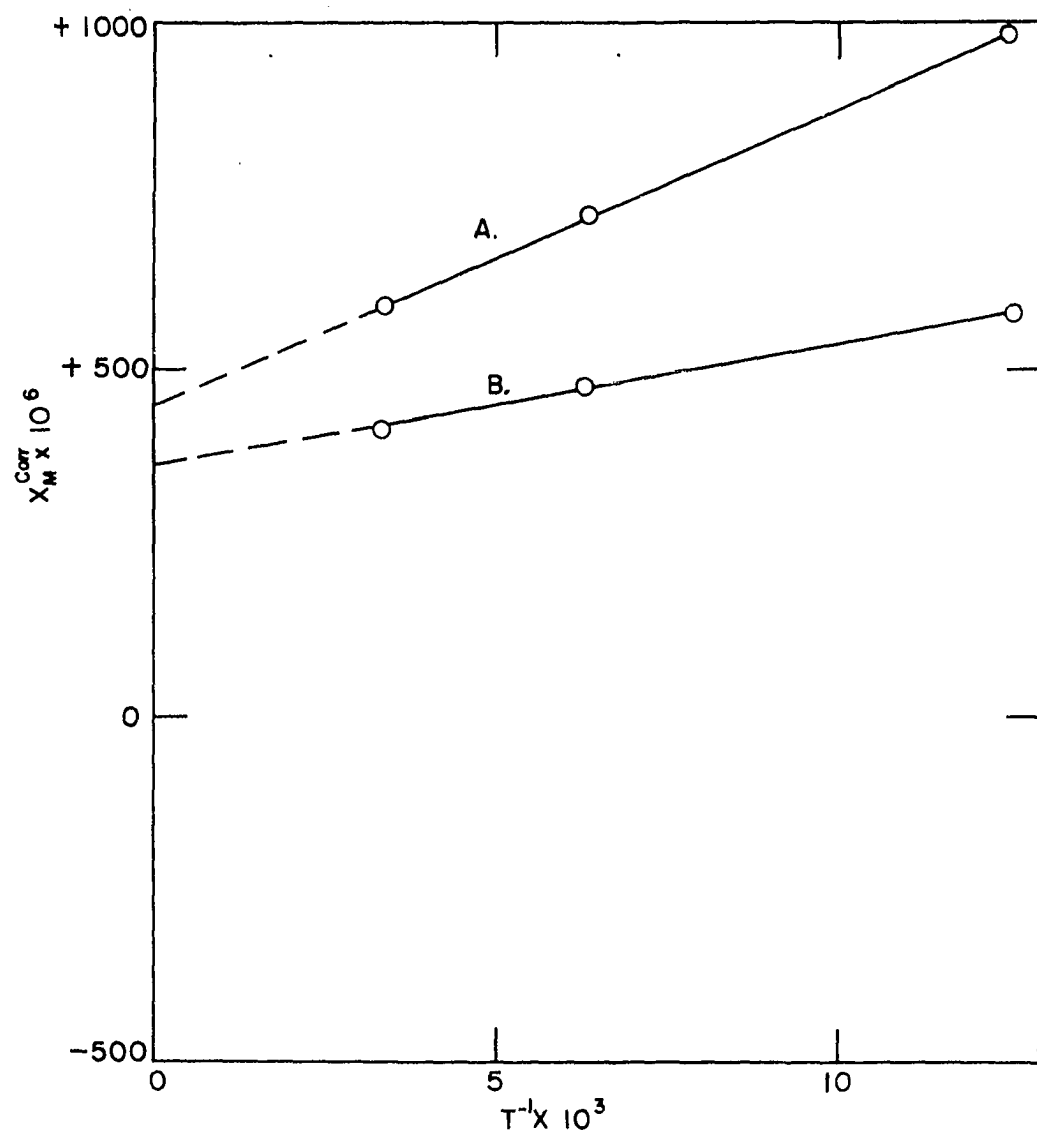
#### Magnetic Susceptibilities

##### Dodeca- $\mu$ -halohexatantalum disulfate hydrates

The magnetic susceptibility data obtained for the disulfates are presented as a plot of  $\chi_M^{\text{corr}}$  versus  $1/T$  in Figure 9. Both apparently obey the Curie law with moments

Figure 9. Magnetic susceptibility data as a plot of  $\chi_M^{\text{corr}}$  vs.  $1/T$  for the dodeca- $\mu$ -halohexatantalum disulfate hydrates







calculated from the slopes, of about 0.4 B.M. and 0.6 B.M. for the chloride and bromide respectively.

Tables 6 and 7 list the calculated values for the effective magnetic moment ( $\mu_{\text{eff}}$ ) and the true magnetic moment ( $\mu$ ) found at each temperature for the chloride and bromide. The values for  $\mu_{\text{eff}}$  were calculated using Equation 10 (40, p. 510).

$$\mu_{\text{eff}} = \sqrt{3k/N} \cdot \sqrt{\chi_M^{\text{corr}} T} \quad (10)$$

where:  $\mu_{\text{eff}}$  = effective magnetic moment, B.M.,

$k$  = Boltzman constant,

$N$  = Avogadro number,

$T$  = absolute temperature,

$\chi_M^{\text{corr}}$  = molar magnetic susceptibility,

corrected for diamagnetism.

The values for  $\mu$  were calculated using Equation 11.

$$\mu = \sqrt{3k/N} \cdot \sqrt{T(\chi_M^{\text{corr}} - N\alpha_p)} \quad (11)$$

where:  $\mu$  = magnetic moment, B.M.,

$k$  = Boltzman constant,

$N$  = Avogadro number,

$T$  = absolute temperature,

$\chi_M^{\text{corr}}$  = molar magnetic susceptibility

corrected for diamagnetism,

Table 6. Calculated values of  $\mu_{\text{eff}}$  and  $\mu$  at each temperature of measurement for the dodeca- $\mu$ -chlorohexatantalum disulfate hydrate

$\chi_M \times 10^6$ , emu/mole	$\chi_M^{\text{corr}} \times 10^6$ , emu/mole <sup>a</sup>	T, °K.	$\mu_{\text{eff}}$ , B.M.	$\mu$ , B.M.
+2	+580	79	0.61	0.37
-102	+476	159	0.78	0.38
-160	+418	300	1.00	0.37

<sup>a</sup>The value for the diamagnetic contribution to the total susceptibility was calculated to be  $-578 \times 10^{-6}$  emu/mole.

Table 7. Calculated values of  $\mu_{\text{eff}}$  and  $\mu$  at each temperature of measurement for the dodeca- $\mu$ -bromohexatantalum disulfate hydrate

$\chi_M \times 10^6$ , emu/mole	$\chi_M^{\text{corr}} \times 10^6$ , emu/mole <sup>a</sup>	T, °K	$\mu_{\text{eff}}$ , B.M.	$\mu$ , B.M.
+308	+988	80	0.80	0.59
+44	+724	157	0.96	0.59
-88	+592	294	1.18	0.58

<sup>a</sup>The value for the diamagnetic contribution to the total susceptibility was calculated to be  $-680 \times 10^{-6}$  emu/mole.

$N\alpha_p$  = temperature independent paramagnetic contribution to the total susceptibility.

The diamagnetic corrections applied to the observed magnetic susceptibilities were large due to the large number of atoms in each mole of these compounds. The values for the temperature independent paramagnetism ( $N\alpha_p$ ) were taken from the intercepts of  $\chi_M^{\text{corr}}$  versus  $1/T$  plots. They were found to be  $+361 \times 10^{-6}$  emu/mole for the chloride and  $+450 \times 10^{-6}$  emu/mole for the bromide. Both compounds were essentially free of ferromagnetic impurities.

#### Dodeca- $\mu$ -halohexatantalum dihalide hydrates

Magnetic susceptibility data for the dihalides,  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2 \cdot 10\text{H}_2\text{O}$  and  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2 \cdot 8\text{H}_2\text{O}$ , are presented in Tables 8 and 9. They apparently obey the Curie law with magnetic moments of about 0.4 B.M. for the chloride and 0.5 B.M. for the bromide. Values for the effective magnetic moment ( $\mu_{\text{eff}}$ ) and the actual magnetic moment ( $\mu$ ) were calculated as discussed for the disulfates.

Values for the temperature independent paramagnetism ( $N\alpha_p$ ) were taken from the intercepts of  $\chi_M^{\text{corr}}$  versus  $1/T$  plots. They were found to be  $+270 \times 10^{-6}$  emu/mole for the chloride and  $+330 \times 10^{-6}$  emu/mole for the bromide. Like the

Table 8. Calculated values for  $\mu_{\text{eff}}$  and  $\mu$  at each temperature of measurement for the dodeca- $\mu$ -chlorohexatantalum dichloride hydrate

$\chi_M \times 10^6$ , emu/mole	$\chi_M^{\text{corr}} \times 10^6$ , emu/mole <sup>a</sup>	T, °K.	$\mu_{\text{eff}}$ , B.M.	$\mu$ , B.M.
+72	+640	65	0.58	0.44
+51	+619	66	0.57	0.43
-40	+528	86	0.60	0.42
-23	+545	85	0.61	0.43
-96	+472	103	0.62	0.41
-220	+348	297	0.91	0.43
-209	+359	298	0.93	0.46

<sup>a</sup>The value for the diamagnetic contribution to the total susceptibility was calculated to be  $-568 \times 10^{-6}$  emu/mole.

Table 9. Calculated values for  $\mu_{\text{eff}}$  and  $\mu$  at each temperature of measurement for the dodeca- $\mu$ -bromohexatantalum dibromide hydrate

$\chi_M \times 10^6$ , emu/mole	$\chi_M^{\text{corr}} \times 10^6$ , emu/mole <sup>a</sup>	T, °K.	$\mu_{\text{eff}}$ , B.M.	$\mu$ , B.M.
+26	+710	86	0.70	0.51
-25	+659	99	0.72	0.51
-222	+426	297	1.01	0.48
-233	+451	299	1.04	0.54

<sup>a</sup>The value for the diamagnetic contribution to the total susceptibility was calculated to be  $-684 \times 10^{-6}$  emu/mole.

disulfates, these compounds were essentially free of ferromagnetic impurities.

#### Discussion of observations on magnetic susceptibilities

The pronounced similarity between the properties of the oxidized and reduced derivatives of the polynuclear units, as discussed earlier for the solution and reflectance spectra, also is noted in the magnetic properties. Oxidized and reduced derivatives of each halide unit,  $\text{Ta}_6\text{X}_{12}^{+2}$  or  $\text{Ta}_6\text{X}_{12}^{+4}$ , have magnetic moments which are nearly the same.

The observation of paramagnetism with Curie behavior and very low moments for the derivatives of the  $\text{Ta}_6\text{X}_{12}^{+2}$  ion does not agree with results reported by other workers. Krylov (37) reported paramagnetic behavior for  $\text{Ta}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$  but found that it obeyed the Curie-Weiss law with  $\theta$  equal to  $-235^\circ\text{K}$ . His values for the molar susceptibility at various temperatures were nearly twice as large as those reported here. On the other hand, LCAO-MO calculations by Cotton and Haas (36) indicated that all bonding levels should be just exactly filled leaving the reduced derivatives diamagnetic.

The magnetic properties reported here present a dilemma which is difficult to resolve. The low moments for the reduced compounds give no indication of the true number

of unpaired electrons per molecule in the absence of knowledge about spin-orbit coupling, which may be important for tantalum compounds. The same statement can be made about the oxidized compounds, but an additional point is raised. The similar values for the moments of both oxidized and reduced derivatives does not necessarily imply a like number of unpaired electrons. However, since there is an even, total number of electrons present in the polynuclear units, the number of unpaired electrons must also be even. If the ground level in the reduced compounds was an orbital triplet containing a total of four electrons then two unpaired electrons would result. Removal of two electrons by oxidation still would leave two electrons unpaired. However, it is not obvious, if this were the case, that the same moment should be exhibited for both the reduced and oxidized states.

It is apparent that further studies of structure, bonding, ground states and spectra must be undertaken before any truly valid explanation for the magnetic properties of the polynuclear tantalum compounds will be possible.

## SUMMARY

The crystalline hydrates,  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2 \cdot 10\text{H}_2\text{O}$  and  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2 \cdot 8\text{H}_2\text{O}$ , were prepared by evaporation of aqueous solutions of  $\text{Ta}_6\text{Cl}_{12}^{+2}$  and  $\text{Ta}_6\text{Br}_{12}^{+2}$  in vacuo. They were found to yield spectra in aqueous solution which were very similar and apparently characteristic of the  $\text{Ta}_6\text{X}_{12}$  unit. Extinction coefficients for observed visible and ultra-violet absorption maxima are given.

A two electron oxidation for the  $\text{Ta}_6\text{Cl}_{12}^{+2}$  and  $\text{Ta}_6\text{Br}_{12}^{+2}$  ions was found and determined quantitatively. Insoluble oxidation products formed in aqueous sulfate solution were identified as  $\text{Ta}_6\text{Cl}_{12}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$  and  $\text{Ta}_6\text{Br}_{12}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ . Both gave infrared absorption spectra indicative of coordination of the sulfate group.

The tetrahalide derivatives,  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_4 \cdot 9\text{H}_2\text{O}$  and  $(\text{Ta}_6\text{Br}_{12})\text{Br}_4 \cdot 5\text{H}_2\text{O}$ , were prepared and identified by analysis. They gave ultraviolet and visible reflectance spectra strikingly similar to the disulfates and dihalides. The most intense absorption band in the spectra varied only about 50 m $\mu$  over the whole range of compounds studied. Infrared absorption studies produced a band at 990  $\text{cm}^{-1}$  for the

tetrabromide which corresponds to the rocking mode for coordinated water. This constitutes the only instance of direct coordination of water by the  $\text{Ta}_6\text{X}_{12}$  unit found in the study.

Oxidation of the polynuclear chloride ion,  $\text{Ta}_6\text{Cl}_{12}^{+2}$ , in hydrochloric acid-methanol solution gave a product with the apparent composition  $\text{Ta}_6\text{Cl}_{17} \cdot x\text{H}_2\text{O}$ . Measurement of conductance, ion exchange studies, and acid-base titrations indicated the material was strongly acidic and contained the  $\text{Ta}_6\text{Cl}_{12}$  unit in an anionic form.

Magnetic susceptibility data for the disulfates,  $(\text{Ta}_6\text{Cl}_{12})(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$  and  $(\text{Ta}_6\text{Br}_{12})(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ , obeyed the Curie law with magnetic moments of 0.4 B.M. for the chloride and 0.6 B.M. for the bromide. The temperature independent paramagnetism was determined as the intercept of  $\chi_M^{\text{corr}}$  versus  $1/T$  plots and gave values of  $+361 \times 10^{-6}$  emu/mole for the chloride and  $+450 \times 10^{-6}$  emu/mole for the bromide. In like manner, the susceptibility data for the dihalides,  $(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2 \cdot 10\text{H}_2\text{O}$  and  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2 \cdot 8\text{H}_2\text{O}$ , obeyed the Curie law with moments of 0.4 B.M. for the chloride and 0.5 B.M. for the bromide. The temperature independent paramagnetism was  $+270 \times 10^{-6}$  emu/mole for the chloride and  $+330 \times 10^{-6}$  emu/mole for the bromide.



## SUGGESTIONS FOR FUTURE WORK

The present study has provided only a beginning look at the varied chemistry of the polynuclear tantalum halides in solution. Much remains to be explored and clarified.

Of primary importance are studies leading to a detailed structure analysis of the various oxidized and reduced derivatives. This, coupled with electron spin resonance data and careful studies of spectra, could provide badly needed information on the energy level arrangement in these compounds. A thorough understanding of the observed magnetic data must wait for such information.

The present work involved study of only the polynuclear tantalum chlorides and bromides. A similar investigation of the reactions and properties of the polynuclear tantalum iodides would be most useful in establishing trends for the halide system. Lower stability of the iodides, toward oxidation and hydrolysis, would present a real challenge. However, their increased reactivity and the lower solubility of many of their salts might provide means for more effective procedures.

Finally, no work has been done to date on the formation

of coordination compounds of the  $\text{Ta}_6\text{X}_{12}$  unit. Improved methods for obtaining pure starting materials should make possible an investigation of a whole series of adducts analogous to those reported in the literature for the polynuclear molybdenum halides.

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